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The Crystal Structure of Some Hexakis(methyl cyanide)metal(II) Tetrachlorometallates(III), M(II)(NCCH$_3$)$_6$[M(III)Cl$_4$]$_2$

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Crystals of Fe^{II})NCCH$_3$)$_6$[Fe^{III}Cl$_4$]$_2$ are trigonal with space group $P3$. The lattice dimensions are $a=11{\cdot}682$ (6) and $c=6{\cdot}134$ (4) Å. Diffractometer data (Mo $K\alpha$ radiation) were used. After correction for twinning (twinning percentage 14·1) anisotropic refinement with 1650 observed reflexions resulted in an R_w value of 0·047. The structure is composed of rows of (FeCl$_4$)$^-$ tetrahedra and Fe(NCCH$_3$)$_6^{2+}$ octahedra. A number of interatomic distances are given. The isomorphous complex Mg(NCCH$_3$)$_6$(AlCl$_4$)$_2$ (photographic Weissenberg data) is discussed and the related compound Ni(NCCH$_3$)$_6$(GaCl$_4$)$_2$ (precession data) is briefly mentioned.

Introduction

Complexes M(II) (NCCH$_3$)$_6$[M(III)Cl$_4$]$_2$ [hereafter M(II)–M(III)], in which M(II) is Mg, Cd or a divalent metal of the first transition series and M(III) is B, Al, Fe, Ga, In or Tl, were investigated by Reedijk & Groeneveld (1968*a*). X-ray powder patterns show that, with the exception of Cu compounds (forming a class by themselves), three different types of structure (*A*, *B*, *C*) occur in this series. Mössbauer measurements, infrared spectra (Reedijk & Groeneveld, 1968*b*), magnetic susceptibilities and e.p.r. spectra (Reedijk, 1969) indicate that the M(II)(NCCH$_3$)$_6^{2+}$ and M(III)Cl$_4^-$ ions have octahedral and tetrahedral shapes respectively, but an exact assignment of the molecular symmetry could not be achieved with these techniques.

It was thought interesting to investigate the exact geometry and symmetry of these complex ions by means of X-ray diffraction, and to establish the relationship between the different polymorphs and the sizes and symmetries of the anions and cations. Since most of the complexes are highly sensitive to moisture, the choice of compounds suitable for X-ray work is limited. The analysis was started with Mg(NCCH$_3$)$_6$ (AlCl$_4$)$_2$ (type *A*), this complex containing relatively light metal atoms. Although its structure could be refined to a reasonable degree of accuracy ($R=0{\cdot}18$), we encountered a number of inconsistencies between calculated and observed structure factors, perhaps due to disorder phenomena (see below). Therefore we decided to analyse Fe(NCCH$_3$)$_6$(FeCl$_4$)$_2$, also belonging to type *A*.

As an example of a *C*-type structure we investigated crystals of Ni(NCCH$_3$)$_6$(GaCl$_4$)$_2$. Its structure is related to that of *A*, but so far no solution could be found. Closely related to type *A* is the structure of Fe(NCH)$_6$ (FeCl$_4$)$_2$ proposed by Constant, Daran & Jeannin (1970). Brief comments on the two structures in relation to the *A*-type structure are given in the present article. The *B*-type structure displays a very intricate powder diffraction pattern and has, so far, not been investigated by us.

Experimental

The complexes were obtained by dissolving stoichiometric amounts of the divalent and trivalent metal chlorides in an excess of methyl cyanide. The Mg–Al compound was prepared using the adduct AlCl$_3$.2CH$_3$CN instead of AlCl$_3$ (Reedijk, 1968). After cooling, the complexes crystallized. The type *A* Mg–Al and Fe–Fe compounds consist of white and green-yellow, hexagonally prismatic crystals respectively. The type *C* Ni–Ga compound consists of pale blue thin hexagonal plates. The crystals were filtered, washed with cold methyl cyanide and dried *in vacuo*. Because of their extreme sensitivity to moisture the crystals were inserted into glass capillaries. After immersion in liquid paraffin, which was dried several times with P$_2$O$_5$, the capillaries were sealed.

Cell dimensions of the Mg–Al compound were determined from zero-layer Weissenberg photographs taken about [010] and [001] with unfiltered copper radiation ($\lambda_{K\alpha1}=1{\cdot}54051$ Å, $\lambda_{K\alpha2}=1{\cdot}54433$ Å, $\lambda_{K\beta}=1{\cdot}39217$ Å) superposed with aluminum powder lines ($a=4{\cdot}0492$ Å at 20°C) for calibration purposes. Non-integrated intensity data were obtained with the equi-inclination Weissenberg method (multiple-film technique) from crystals mounted about [001] and [010] using Ni-filtered Cu $K\alpha$ radiation. Intensities from six levels about [001] ($l=0$ up to 5) and ten levels about [010] ($k=0$ up to 9) were estimated visually and reduced to structure-factor moduli in the usual way. An absorption correction was applied to the c axis data, assuming a cylindrical cross-section for the crystal used ($r\simeq0{\cdot}02$ cm, $\mu r=1{\cdot}6$). On the basis of the b-axis data, the c-axis data comprising 821 symmetry-independent reflexions (including 126 non-observed ones) were put on a common scale. Non-observed reflexions were given intensity values equal to the lowest measured intensity.

The lattice parameters, as well as the X-ray intensity data of the Fe–Fe compound, were measured on a Nonius three-circle diffractometer using Zr-filtered Mo $K\alpha$ radiation (λ=0·71069 Å). According to the classification rules of Arndt & Willis (1966) the goniostat has normal-beam equatorial diffraction geometry, with χ-motion restricted between 0 and $-90°$. A hexagonally prismatic crystal with approximate dimensions 0·15×0·15×0·6 mm was mounted about [001]. The intensities were collected by means of the θ–2θ scan mode to a maximum θ value of 35°; high intensities were reduced by using attenuation filters. The background intensity was measured at each side of a reflexion for half the scanning time. A reflexion was considered significant if the net count exceeded twice the standard deviation. The number of observed symmetry-dependent reflexions having positive glancing angles was 2374 and that with negative values 341. An absorption correction was applied according to the Monte Carlo method as programmed by de Graaff (1972). The repeated measurements of a number of standard reflexions ensured the correction for the decrease in scattering power of the crystal by means of a polynomial function of the exposure time. An average was taken of the symmetry-dependent reflexions and all data were reduced to structure factors in the usual way. A total of 1755 observed reflexions remained including 266 pairs hkl and $\bar{h}\bar{k}\bar{l}$, and 595 non-observed ones including 31 pairs hkl and $\bar{h}\bar{k}\bar{l}$.

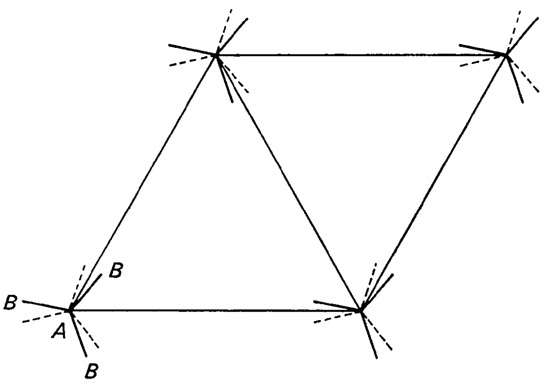

Fig. 1. A simplified model for disorder or twinning: the orientation of AB_3 groups about the threefold rotation axis z in the Fe–Fe structure. The solid lines alone represent the ordered structure; the solid and dashed lines in statistical distribution the disorder; the solid lines in one part of the lattice and the dashed lines in another part of the crystal describe the twinned structure.

The cell dimensions of the Ni–Ga compound were determined with Mo $K\alpha$ radiation from $hk0$ and $0kl$ precession photographs. Film shrinkage was corrected for.

Both the symmetry relations in reciprocal space and the Patterson function of the compounds Mg–Al and Fe–Fe exclude all space groups except $P3$ and $P\bar{3}$. For the present the space group $P3$ was assumed; an R_w-ratio test (Hamilton, 1965) justified this assumption. Crystals of the Mg–Al compound floated on CCl_4 (density of 1·6 g.cm^{-3}). Hence the unit cell contains one formula unit Mg–Al.

The Ni–Ga complex has the space group $P3$ or $P\bar{3}$. The cell volume is about six times that of the Fe–Fe compound [a(Ni–Ga)$\simeq a$(Fe–Fe)$\sqrt{3}$; c(Ni–Ga)$\simeq 2c$(Fe–Fe)]. Reflexions with $h-k=3n\pm1$ are not present if $l=0$ or $l=2n+1$, and are always weak; this indicates a subcell with dimensions of the Fe–Fe compound. Crystal data for the three compounds are given in Table 1.

Structure determination and refinement

The presence of one formula unit of the M(II)–M(III) compound in a unit cell with symmetry $P3$ requires that the three metal ions and two chlorine ions Cl(2) and Cl(4) be in the special positions $0,0,z$, $\frac{1}{3},\frac{2}{3},z$ and $\frac{2}{3},\frac{1}{3},z$. The remaining ions Cl(1), Cl(3) and the ligand atoms are accommodated in general positions. An approximate model for the structure of the Mg–Al compound was derived from a Patterson map and successive Fourier syntheses. The Patterson function of the Fe–Fe compound showed that the two structures were isomorphous.

During the least-squares refinement of the Fe–Fe and Mg–Al structures, the following scattering factors were used: (1) the values for Fe^{2+}, Fe^{3+} and Cl^- ions evaluated by Cromer & Waber (1965), (2) those for Mg^{2+}, Al^{3+}, N and C (valence) from *International Tables for X-ray Crystallography* (1962), all values except those for nitrogen and carbon being corrected for the real part of the anomalous scattering. The imaginary part of the scattering factor was not taken into account.

Table 1. *Unit-cell parameters of three compounds* $M(II)(NCCH_3)_6[M(III)Cl_4]_2$

The numbers in brackets are estimated standard deviations in terms of the last decimal given.

M(II)–M(III)	Mg–Al	Fe–Fe	Ni–Ga
Space group	$P3$	$P3$	$P3$ or $P\bar{3}$
a	11·693 (5)	11·682 (6)	20·526 (4) Å
c	6·151 (3)	6·134 (4)	11·879 (3) Å
d(calc)	1·387	1·597	1·637 g.cm^{-3}
V	728·3	725·0	4334·4 Å^3
Z	1	1	6
μ	86 (Cu $K\alpha$)	22·5 (Mo $K\alpha$)	33·4 cm^{-1} (Mo $K\alpha$)

I. *The* Fe–Fe *compound*

As a starting point for the Fe–Fe compound the Mg–Al model was used. The weights used during the refinements were $w(F_o)=[\sigma(F_o)]^{-2}$. Refining all atoms except hydrogen in four cycles with an overall temperature factor and in four cycles with individual isotropic temperature factors reduced the reliability index R to 0·110 (omitting non-observed reflexions) and the weighted index R_w to 0·138, where

$$R=|F_o-F_c/S|/\sum F_o$$

and

$$R_w=[\sum w(F_o)\,(F_o-F_c/S)^2/\sum w(F_o)F_o^2]^{1/2}.$$

The scaling factor $1/S$ reduces F_c to the scale of F_o. A refinement with anisotropic temperature factors during 5 cycles was executed and the R index dropped to 0·079, and R_w to 0·097.

On inspection of the agreement between observed and calculated structure factors, large discrepancies were detected in some cases. For reflexions with $h\neq k$ we observed that $||F_o(hkl)|-|F_o(khl)||<||F_c(hkl)|-|F_c(khl)||$. Accepting the model as essentially correct the discrepancies occurring may be due either to disorder or to twinning. The first case would involve a mixing of positions x, y, z and y, x, z, the second a mixing of reflexions hkl and khl (Fig. 1).

The disorder, or twinning, concerns atoms distributed over positions x, y, z and y, x, z. In the case of

Table 2. *Observed (corrected for a twinning factor of* 0·141) *and calculated structure factors on an absolute scale* (×100)

The non-observed reflexions are indicated by an asterisk.
The reflexions treated as non-observed are indicated by negative F_o values. A complete list including the A and B parts is available upon request.

H	K	L	FO	FC
-2	4	0	1580	1738
2	-4	0	1579	1738
-3	6	0	4883	4863
3	-6	0	4886	4863
-4	8	0	2757	2733
4	-8	0	2771	2733
-5	10	0	3135	3049
5	-10	0	3104	3049
-6	12	0	2755	2700
6	-12	0	2780	2700
-7	14	0	823	838
7	-14	0	824	838
-8	16	0	696	609
8	-16	0	647	609
9	-18	0	469	445
1	1	1	9572	8290
-1	-1	-1	9452	8290
-1	2	1	5086	4152
1	-2	-1	4755	4152
2	2	1	1770	1447
-2	-2	-1	1713	1447
3	3	1	1540	1535
-3	-3	-1	1416	1535
-2	4	1	2342	2003
2	-4	-1	2277	2003
4	4	1	1563	1561
-4	-4	-1	1498	1561
5	5	1	1940	1925
-3	6	1	1627	1489
3	-6	-1	1549	1489
6	6	1	2035	2009
7	7	1	329	357
-4	8	1	820	887
4	-8	-1	750	887
8	8	1	494	482
9	9	1	404	425
-5	10	1	2778	2822
-6	12	1	1558	1473
-7	14	1	695	696
-8	16	1	549	626
0	0	2	8206	8142
0	0	-2	8080	8142
1	1	2	2185	2092
-1	-1	-2	1951	2092
-1	2	2	8785	8503
1	-2	-2	8532	8503
2	2	2	2531	2527
-2	-2	-2	2491	2527
3	3	2	6087	5975
-3	-3	-2	6118	5975
-2	4	2	5862	5875
2	-4	-2	5781	5875
4	4	2	2510	2495
5	5	2	2116	2031
-3	6	2	3198	3275
3	-6	-2	3182	3275
6	6	2	1611	1615
7	7	2	461	465
-4	8	2	1233	1194
8	8	2	412	416
9	9	2	488	464
-5	10	2	2522	2497
-6	12	2	1585	1515
-7	14	2	534	506
-8	16	2	698	672
0	0	3	5215	5158
0	0	-3	5115	5158
1	1	3	2576	2583
-1	-1	-3	2528	2583
-1	2	3	4702	4629
1	-2	-3	4571	4629
2	2	3	1229	1208
-2	-2	-3	1267	1208
3	3	3	3233	3207
-3	-3	-3	3207	3207
-2	4	3	7772	7883
2	-4	-3	7894	7883
4	4	3	4281	4372
5	5	3	1534	1575
-3	6	3	1854	1823
3	-6	-3	1841	1823
6	6	3	735	665
7	7	3	421	452
-4	8	3	519	495
8	8	3	295	308
-5	10	3	1896	1916
-6	12	3	773	806
-7	14	3	346	309
-8	16	3	665	594
0	0	4	1041	1138
0	0	-4	1053	1138
1	1	4	187	308
-1	-1	-4	212	308
-1	2	4	2402	2441
1	-2	-4	2414	2441
2	2	4	951	945
3	3	4	646	655
-2	4	4	3261	3163
4	4	4	1998	2000
5	5	4	608	708
-3	6	4	874	927
6	6	4	472	507
7	7	4	121	58*
-4	8	4	163	157*
8	8	4	179	186*
-5	10	4	362	430
-6	12	4	128	71*
-7	14	4	535	474
-8	16	4	366	358
0	0	5	1387	1366
1	1	5	1773	1811
-1	2	5	2362	2345
2	2	5	793	802
3	3	5	2299	2261
-2	4	5	3351	3486
4	4	5	1546	1593
5	5	5	251	315
-3	6	5	1541	1508
6	6	5	525	488
7	7	5	517	535
-4	8	5	346	377
8	8	5	185	134*
-5	10	5	659	675
-6	12	5	405	316
-7	14	5	545	498
-8	16	5	185	240*
0	0	6	1342	1407
1	1	6	562	671
-1	2	6	301	300
2	2	6	369	339
3	3	6	479	454
-2	4	6	600	671
4	4	6	358	390
5	5	6	270	280
-3	6	6	518	582
6	6	6	171	294*
7	7	6	182	203*
-4	8	6	408	361
-5	10	6	219	97*
-6	12	6	171	151*
-7	14	6	182	101*
0	0	7	490	403
1	1	7	222	58
-1	2	7	112	77*
2	2	7	688	700
3	3	7	366	415
-2	4	7	352	358
4	4	7	295	342
5	5	7	198	165*
-3	6	7	392	378
6	6	7	181	83*
-4	8	7	583	557
-5	10	7	171	112*
-6	12	7	181	168*
0	0	8	673	722
1	1	8	317	156
-1	2	8	207	209*
2	2	8	337	395
3	3	8	169	140*
-2	4	8	164	220*
4	4	8	175	80*
5	5	8	183	93*
-3	6	8	277	236*
-4	8	8	175	159*
-5	10	8	183	50*
0	0	9	495	540
1	1	9	377	398
-1	2	9	357	323
2	2	9	196	173*
3	3	9	165	186*
-2	4	9	289	339*
-3	6	9	292	205
0	2	0	2133	2175
0	-2	0	2135	2175
0	3	0	8232	7376
0	-3	0	8293	7376
0	4	0	320	435
0	-4	0	433	435*
0	5	0	904	921
0	-5	0	935	921
0	6	0	9747	9524
0	-6	0	9693	9524
0	7	0	317	206
0	-7	0	437	206*
0	8	0	362	499
0	-8	0	358	499
0	9	0	2374	2433
0	-9	0	2384	2433
0	10	0	484	395
0	-10	0	496	395
0	11	0	407	369
0	-11	0	489	369
0	12	0	1744	1711
0	-12	0	1729	1711
0	13	0	358	401
0	-13	0	370	401
0	14	0	187	126
0	-14	0	240	126*
0	15	0	374	408
0	-15	0	407	408
0	16	0	164	100
0	-16	0	192	100*
-2	3	0	2769	2916
2	-3	0	2803	2916
-1	3	0	4340	4554
1	-3	0	4370	4554
-3	4	0	5409	5158
3	-4	0	5423	5158
-1	4	0	2217	2202
1	-4	0	2259	2202
-4	5	0	7080	6876
4	-5	0	7072	6876
-1	5	0	9332	9414
1	-5	0	9417	9414
-3	5	0	950	898
3	-5	0	961	898
-2	5	0	3553	3447
2	-5	0	3595	3447
-5	6	0	2170	2238
5	-6	0	2173	2238
-1	6	0	657	591
1	-6	0	692	591
-4	6	0	420	407
4	-6	0	402	407
-2	6	0	2278	2298
2	-6	0	2297	2298
-6	7	0	560	572
6	-7	0	552	572
-1	7	0	244	258
1	-7	0	259	258
-5	7	0	3598	3730
5	-7	0	3630	3730
-2	7	0	5459	5697
2	-7	0	5557	5697
-4	7	0	2595	2612
4	-7	0	2591	2612
-3	7	0	1038	1077
3	-7	0	1053	1077
-7	8	0	2988	2892
7	-8	0	2938	2892
-1	8	0	3798	3769
1	-8	0	3767	3769
-6	8	0	-178	620
6	-8	0	-214	620
-2	8	0	777	760
2	-8	0	778	760
-5	8	0	1858	1871
5	-8	0	1882	1871
-3	8	0	544	645
3	-8	0	553	645
-8	9	0	1412	1374
8	-9	0	1400	1374
-1	9	0	923	934
1	-9	0	857	934
-7	9	0	1050	1020
7	-9	0	1048	1020
-2	9	0	1544	1452
2	-9	0	1503	1452
-6	9	0	2999	3095
6	-9	0	3012	3095
-3	9	0	2447	2468
3	-9	0	2391	2468
-5	9	0	478	484
5	-9	0	492	484
-4	9	0	398	549
4	-9	0	339	549
-9	10	0	1063	1052
9	-10	0	1062	1052
-1	10	0	294	372
1	-10	0	251	372
-8	10	0	1481	1433
8	-10	0	1480	1433
-2	10	0	1588	1570
2	-10	0	1576	1570
-7	10	0	-92	269
7	-10	0	-235	269
-3	10	0	1590	1645
3	-10	0	1593	1645
-6	10	0	1200	1112
6	-10	0	1194	1112
-4	10	0	350	341
4	-10	0	287	341
-10	11	0	1638	1545
10	-11	0	1589	1545
-1	11	0	2090	2068
1	-11	0	2124	2068
-9	11	0	-194	163
9	-11	0	-52	163
-2	11	0	804	747
2	-11	0	804	747
-8	11	0	611	656
8	-11	0	583	656
3	-11	0	-220	25
-3	11	0	203	25*
-7	11	0	2983	2972
7	-11	0	2954	2972
-4	11	0	1897	1868
4	-11	0	1491	1468
-6	11	0	672	581
6	-11	0	657	581
-5	11	0	1071	1037
5	-11	0	1089	1037
-11	12	0	665	768
11	-12	0	703	768
-1	12	0	-199	122
1	-12	0	-160	122
-10	12	0	568	531
10	-12	0	511	531
-2	12	0	795	824
2	-12	0	803	824
-9	12	0	1764	1797
9	-12	0	1777	1797
-3	12	0	1617	1552
3	-12	0	1561	1552
-8	12	0	396	447
8	-12	0	329	447
-4	12	0	543	605
4	-12	0	618	605
-7	12	0	136	51
7	-12	0	190	51*
-5	12	0	329	347
5	-12	0	273	347
-12	13	0	230	91
12	-13	0	202	91*
-1	13	0	405	434
1	-13	0	432	434
-11	13	0	754	686
11	-13	0	749	686
-2	13	0	1506	1445
2	-13	0	1529	1445
-10	13	0	365	292
10	-13	0	292	292
-3	13	0	165	129
3	-13	0	152	129*
-9	13	0	815	786
9	-13	0	799	786
-4	13	0	419	466
4	-13	0	415	466
-8	13	0	1483	1425
8	-13	0	1485	1425
-5	13	0	1450	1379
5	-13	0	1394	1379
7	-13	0	172	107
-7	13	0	241	107
-6	13	0	546	562
6	-13	0	578	562
-13	14	0	591	579
13	-14	0	576	579
-1	14	0	806	770
1	-14	0	804	770
-12	14	0	203	199
12	-14	0	193	189*
-2	14	0	136	205
2	-14	0	165	205*
-11	14	0	159	208
11	-14	0	168	208*
3	-14	0	150	91
-3	14	0	270	91
-10	14	0	776	753
10	-14	0	718	753
-4	14	0	598	668
4	-14	0	679	668
-9	14	0	397	495
9	-14	0	413	495
-5	14	0	254	513
5	-14	0	391	513
-8	14	0	117	101
8	-14	0	158	101*
-6	14	0	282	365
6	-14	0	173	365*
-14	15	0	291	191
14	-15	0	326	191
-1	15	0	159	318
1	-15	0	188	318*
13	-15	0	162	209
-13	15	0	298	209
-2	15	0	330	342
2	-15	0	353	342
-12	15	0	716	631
12	-15	0	704	631
-3	15	0	472	489
3	-15	0	461	489
-11	15	0	128	106
11	-15	0	136	106*
-4	15	0	124	128
4	-15	0	187	128*
-10	15	0	179	187
10	-15	0	264	187
-5	15	0	122	32
5	-15	0	154	32*
-9	15	0	595	662
9	-15	0	664	662
-6	15	0	653	642
6	-15	0	626	642
-8	15	0	496	450
8	-15	0	545	450
-7	15	0	124	146
7	-15	0	171	146*
-15	16	0	361	137
15	-16	0	195	137*
-1	16	0	181	92
1	-16	0	131	92*
-14	16	0	576	444
14	-16	0	429	444
-2	16	0	403	333
2	-16	0	411	333
-13	16	0	130	160
13	-16	0	212	160*
-3	16	0	132	234
3	-16	0	144	234*
-12	16	0	315	272
12	-16	0	322	272
-4	16	0	275	195
4	-16	0	143	195*
-11	16	0	744	535
11	-16	0	674	535
-5	16	0	727	604
5	-16	0	675	604
-10	16	0	232	34
10	-16	0	209	34*
-6	16	0	336	375
6	-16	0	335	375
-9	16	0	302	205
9	-16	0	282	205
-7	16	0	186	123
7	-16	0	186	123*
15	-17	0	185	35*
2	-17	0	185	100*
14	-17	0	169	153*
3	-17	0	174	95*
13	-17	0	693	636
4	-17	0	507	355
12	-17	0	154	122*
5	-17	0	336	63
11	-17	0	183	133*
6	-17	0	269	29*
10	-17	0	676	626
7	-17	0	656	566
9	-17	0	238	40*
8	-17	0	194	142*
13	-18	0	185	140*
5	-18	0	185	34*
12	-18	0	337	345
6	-18	0	561	473
11	-18	0	182	125*
7	-18	0	153	73*
10	-18	0	322	230*
8	-18	0	275	140*
-3	2	1	5484	5571
3	-2	-1	5375	5571
1	2	1	7729	7835
-1	-2	-1	7574	7835
-2	2	1	2298	2057
2	-2	-1	2215	2057
0	2	1	4735	4668
0	-2	-1	4639	4668
-5	3	1	3001	2993
5	-3	-1	2943	2993
2	3	1	1840	1803
-2	-3	-1	1793	1803
-4	3	1	2677	2584
4	-3	-1	2665	2584
1	3	1	4396	4001
-1	-3	-1	4193	4001
-3	3	1	1518	1140
3	-3	-1	1245	1140
0	3	1	1493	1081
0	-3	-1	1009	1081
-2	3	1	6434	6115
2	-3	-1	6366	6115
-1	3	1	7958	7591
1	-3	-1	7792	7591
-7	4	1	3256	3114
7	-4	-1	3222	3114
3	4	1	3669	3670
-3	-4	-1	3618	3670
-6	4	1	938	1077
6	-4	-1	972	1077
2	4	1	2359	2423
-2	-4	-1	2316	2423
-5	4	1	6438	6243
5	-4	-1	6189	6243
1	4	1	5067	4998
-1	-4	-1	4969	4998
-4	4	1	1763	1630
4	-4	-1	1727	1630
0	4	1	-119	120
0	-4	-1	-111	120
-3	4	1	6686	6459
3	-4	-1	6513	6459
-1	4	1	3242	3201
1	-4	-1	3168	3201
-9	5	1	335	555
4	5	1	1787	1838
-8	5	1	1157	1293
8	-5	-1	1195	1253
3	5	1	2636	2561
-3	-5	-1	2515	2561
-7	5	1	5106	5008
7	-5	-1	4877	5008
2	5	1	3265	3204
-2	-5	-1	3206	3204
-6	5	1	541	607
6	-5	-1	523	607
1	5	1	686	710
-1	-5	-1	634	710
-5	5	1	1549	1555
5	-5	-1	1500	1555
0	5	1	400	443
0	-5	-1	390	443
-4	5	1	3905	3777
4	-5	-1	3828	3777
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1	-5	-1	4945	4878
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3	-5	-1	3915	3864
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2	-5	-1	3931	3827
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5	6	1	111	245*
-10	6	1	329	351
4	6	1	273	128
-9	6	1	339	515
3	6	1	644	544
-8	6	1	1942	1950
2	6	1	715	921
-7	6	1	267	482
7	-6	-1	335	482
1	6	1	2197	2109
-1	-6	-1	2127	2109
-6	6	1	4792	4758
6	-6	-1	4657	4758
0	6	1	5711	5546
0	-6	-1	5498	5546
-5	6	1	394	553
5	-6	-1	401	553
-1	6	1	1521	1522
1	-6	-1	1502	1522
-4	6	1	356	534
4	-6	-1	368	534
-2	6	1	737	834
2	-6	-1	659	834
-13	7	1	711	821
6	7	1	-85	142
-12	7	1	-211	386
5	7	1	233	292
-11	7	1	1348	1332
4	7	1	2480	2469
-10	7	1	526	508
3	7	1	264	411
-9	7	1	1341	1324
2	7	1	337	505
-8	7	1	2187	2239
1	7	1	1787	1887
-7	7	1	849	903
7	-7	-1	847	903
0	7	1	708	781
0	-7	-1	703	781
6	-7	-1	-187	417
-6	7	1	267	417
1	-7	-1	-219	297
-1	7	1	267	297
-5	7	1	2281	2357
5	-7	-1	2227	2357
-2	7	1	3566	3632
2	-7	-1	3420	3632
-4	7	1	1556	1584
4	-7	-1	1534	1584
-3	7	1	2059	2147
3	-7	-1	2040	2147
-15	8	1	246	204
7	8	1	270	159
-14	8	1	-219	316
6	8	1	528	458
-13	8	1	970	958
5	8	1	996	1083
-12	8	1	833	737
4	8	1	350	903
-11	8	1	390	427
3	8	1	566	523
-10	8	1	757	801
2	8	1	779	851
-9	8	1	1203	1229
1	8	1	1264	1244
-8	8	1	1064	1124
0	8	1	1503	1503
-7	8	1	1809	1814
-1	8	1	1982	2035
-6	8	1	1735	1630
-2	8	1	1187	1149
-5	8	1	1669	1754
5	-8	-1	1641	1754
-3	8	1	1796	1666
3	-8	-1	1703	1666
-17	9	1	175	118*
8	9	1	125	93*
-16	9	1	168	207*
7	9	1	160	90*
-15	9	1	498	466
6	9	1	255	194
-14	9	1	721	732
5	9	1	-201	159
-13	9	1	644	652
4	9	1	859	872
-12	9	1	1691	1695
3	9	1	1186	1128
-11	9	1	1080	1101
2	9	1	-22	132
-10	9	1	-73	81
1	9	1	995	1006
-9	9	1	756	912
0	9	1	739	766
-8	9	1	2613	2599
-1	9	1	1113	1089
-7	9	1	1326	1288
-2	9	1	2651	2558
-6	9	1	1733	1724
-3	9	1	1692	1647
-5	9	1	1687	1716
-4	9	1	-61	164
-18	10	1	182	133*
8	10	1	182	220*
-17	10	1	559	602
7	10	1	515	526
-16	10	1	168	49*
6	10	1	168	262*
-15	10	1	137	223*
5	10	1	245	262*
-14	10	1	525	534
4	10	1	553	455
-13	10	1	612	697
3	10	1	532	584
-12	10	1	-196	285
2	10	1	982	974
-11	10	1	2127	2065
1	10	1	2034	2024
-10	10	1	126	119*
0	10	1	447	485
-9	10	1	1179	1180
-1	10	1	469	477
-8	10	1	2021	2092
-2	10	1	1270	1253
-7	10	1	1395	1391
-3	10	1	1113	1093
-6	10	1	388	277
-4	10	1	1695	1729
-18	11	1	183	55*
7	11	1	183	180*
-17	11	1	176	18*
6	11	1	176	116*
-16	11	1	442	286
5	11	1	732	699
-15	11	1	164	249*
4	11	1	121	4*
-14	11	1	116	186*
3	11	1	415	310
-13	11	1	1131	1201
2	11	1	742	731
-12	11	1	247	243
1	11	1	300	394
-11	11	1	-218	313
0	11	1	430	408
-10	11	1	724	733
-1	11	1	1684	1633
-9	11	1	-163	136
-2	11	1	931	909
-8	11	1	500	656
-3	11	1	695	593
-7	11	1	2209	2243
-4	11	1	1687	1693
-6	11	1	506	500
-5	11	1	561	569
-18	12	1	184	332*
6	12	1	411	278
-17	12	1	178	95*
5	12	1	178	99*
-16	12	1	172	108*
4	12	1	137	92*
-15	12	1	221	137*
3	12	1	298	206
-14	12	1	285	372
2	12	1	288	284
-13	12	1	235	107
1	12	1	390	382
-12	12	1	999	869
0	12	1	1212	1168
-11	12	1	132	372*
-1	12	1	334	371
-10	12	1	-214	144
-2	12	1	362	452
-9	12	1	429	479
-3	12	1	438	528
-8	12	1	176	49*
-4	12	1	317	231
-7	12	1	340	489
-5	12	1	132	141*
-18	13	1	186	60*
5	13	1	186	82*
-17	13	1	348	332
4	13	1	444	402
-16	13	1	210	236*
3	13	1	170	120*
-15	13	1	283	259
2	13	1	269	123*
-14	13	1	361	410
1	13	1	251	264*
-13	13	1	355	441
0	13	1	310	171
-12	13	1	115	334*
-1	13	1	146	144*
-11	13	1	607	630
-2	13	1	957	912
-10	13	1	347	270
-3	13	1	243	485
-9	13	1	364	390
-4	13	1	105	24*
-8	13	1	967	928
-5	13	1	360	410
-7	13	1	445	443
-6	13	1	380	479
-17	14	1	133	110*
3	14	1	183	70*
-16	14	1	348	381
2	14	1	416	414
-15	14	1	358	276
1	14	1	230	265*
-14	14	1	273	208
0	14	1	301	398
-13	14	1	610	572
-1	14	1	437	393
-12	14	1	669	640
-2	14	1	161	109*
-11	14	1	-171	325
-3	14	1	657	566
-10	14	1	380	271
-4	14	1	611	666
-9	14	1	671	669
-5	14	1	356	322
-8	14	1	-138	106
-6	14	1	560	480
-17	15	1	156	166*
2	15	1	186	75*
-16	15	1	181	103*
1	15	1	181	239*
-15	15	1	325	308*
0	15	1	404	425
-14	15	1	286	368*
-1	15	1	173	35*
-13	15	1	272	138*
-2	15	1	401	389
-12	15	1	788	798
-3	15	1	538	544
-11	15	1	283	399
-4	15	1	177	32*
-10	15	1	319	328
-5	15	1	556	549
-9	15	1	694	655
-6	15	1	431	502
-8	15	1	889	861
-7	15	1	367	257
-16	16	1	185	93*
0	16	1	185	115*
-15	16	1	181	140*
-1	16	1	181	94*
-14	16	1	527	499
-2	16	1	178	224*
-13	16	1	175	197*
-3	16	1	175	149*
-12	16	1	172	112*
-4	16	1	311	395
-11	16	1	736	662
-5	16	1	746	721
-10	16	1	168	198*
-6	16	1	168	77*
-9	16	1	363	218
-7	16	1	166	159*
-1	1	2	6837	6884
1	-1	-2	6756	6884
0	1	2	1030	992
0	-1	-2	1005	992
-3	2	2	2855	2625
3	-2	-2	2738	2625
1	2	2	4323	3959
-1	-2	-2	4227	3959
-2	2	2	293	68
0	2	2	237	304
-5	3	2	1538	1574
5	-3	-2	1545	1574
2	3	2	3398	3422
-2	-3	-2	3417	3422
-4	3	2	1929	1925
4	-3	-2	1802	1925

disorder the distribution is statistical and would result in the symmetry *P*31*m* for a 1:1 arrangement. The twinned structure arises from the configuration *x*, *y*, *z* in one part of the lattice and the configuration *y*, *x*, *z* in another part. In this case (100) acts as mirror plane for the separate individuals. The justification for these assumptions can be seen in Fig. 2, the ultimate structure. All atoms in general positions are located near one of the planes $\{30\bar{3}0\}$ and only small rotations are required to obtain the mirror configuration. In both models an extra parameter, the occupation number *p* $(0 \le p \le 1)$, is introduced for occupation of position *x*, *y*, *z* with contribution $1-p$ and position *y*, *x*, *z* with contribution *p*.

(*a*) Disorder

The contributions to the calculated structure factor F'_c are coherent and have to be added according to

$$F'_c = F_c(x,y,z) + F_c(y,x,z)$$
$$= (1-p) \sum_{j}^{N} f_j \exp\left[2\pi i(hx_j + ky_j + lz_j)\right]$$
$$+ p \sum_{j}^{N} f_j \exp\left[2\pi i(hy_j + kx_j + lz_j)\right] . \qquad (1)$$

Corresponding to the choice of origin $(0,0,0, \frac{2}{3}, \frac{1}{3}, 0,$ or $\frac{1}{3}, \frac{2}{3}, 0)$ there are three possibilities for introducing disorder by means of a pseudo-mirror plane: through the $Fe(NCCH_3)_6$ octahedron, or through either one of the two $FeCl_4$ tetrahedra. Difference maps calculated after isotropic and anisotropic 'ordered' refinements indicated that the first possibility (exchange of the two $FeCl_4$ tetrahedra) was unlikely.

The refinement was executed with coupled atoms at *x*, *y*, *z* and *y*, *x*, *z*, having equal isotropic thermal par-

Table 2 (*cont.*)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FC	FC	H	K	L	FO	FC
1	3	2	2110	2117	2	-7	-2	3148	3116	-8	11	2	712	400*	-5	16	2	699	645
-1	-3	-2	2054	2117	-4	7	2	1406	1424	-3	11	2	370	415	-10	16	2	171	205*
-3	3	2	6003	5820	4	-7	-2	1410	1424	-7	11	2	2443	2494	-6	16	2	171	67*
3	-3	-2	5939	5820	-3	7	2	1320	1405	-4	11	2	1916	1861	-9	16	2	504	377
0	3	2	4928	4751	3	-7	-2	1344	1405	-6	11	2	439	430	-7	16	2	170	295*
0	-3	-2	4735	4751	-15	8	2	351	429	-5	11	2	250	366*	-1	1	3	-217	243
-2	3	2	3830	3800	7	8	2	289	310	-18	12	2	350	253	1	-1	-3	-193	243
2	-3	-2	3793	3800	-14	8	2	477	544	6	12	2	395	462	0	1	3	1674	1624
-1	3	2	2468	2367	6	8	2	325	405	-17	12	2	180	84*	0	-1	-3	1670	1624
1	-3	-2	2338	2367	-13	8	2	1080	957	5	12	2	180	51*	-3	2	3	4287	4357
-7	4	2	1133	1236	5	8	2	864	817	-16	12	2	175	275*	3	-2	-3	4248	4357
7	-4	-2	1149	1236	-12	8	2	587	684	4	12	2	175	141*	1	2	3	3356	3270
3	4	2	2603	2608	4	8	2	350	410	-15	12	2	329	262	-1	-2	-3	3340	3270
-3	-4	-2	2580	2608	-11	8	2	577	651	3	12	2	515	552	-2	2	3	4037	3990
-6	4	2	-87	755	3	8	2	256	490	-14	12	2	163	190*	2	-2	-3	3908	3990
6	-4	-2	-187	755	-10	8	2	1096	1081	2	12	2	121	203*	0	2	3	3315	3391
2	4	2	2341	2215	2	8	2	1539	1546	-13	12	2	282	221	0	-2	-3	3337	3391
-2	-4	-2	2319	2215	-9	8	2	826	929	1	12	2	208	235*	-5	3	3	3692	3687
-5	4	2	3599	3595	1	8	2	1093	1132	-12	12	2	816	796	5	-3	-3	3687	3687
5	-4	-2	3553	3595	-8	8	2	1438	1422	0	12	2	951	916	2	3	3	2132	2234
1	4	2	3456	3392	0	8	2	-115	417	-11	12	2	235	179	-2	-3	-3	2107	2234
-1	-4	-2	3437	3392	-7	8	2	2787	2792	-1	12	2	332	143	-4	3	3	1857	1934
-4	4	2	797	793	-1	8	2	2064	2065	-10	12	2	619	587	4	-3	-3	1893	1934
4	-4	-2	802	793	-6	8	2	1314	1445	-2	12	2	-147	240	1	3	3	4231	4299
0	4	2	355	275	-2	8	2	364	401	-9	12	2	544	509	-1	-3	-3	4225	4299
0	-4	-2	321	275	-5	8	2	1272	1271	-3	12	2	1199	1237	-3	3	3	4364	4223
-3	4	2	3898	3774	-3	8	2	1267	1363	-8	12	2	376	460	3	-3	-3	4314	4223
3	-4	-2	3798	3774	-17	9	2	177	108*	-4	12	2	211	220*	0	3	3	2877	2814
-1	4	2	1664	1535	8	9	2	177	57*	-7	12	2	538	548	0	-3	-3	2851	2814
1	-4	-2	1700	1535	-16	9	2	170	59*	-5	12	2	397	383	-2	3	3	5406	5268
-9	5	2	603	796	7	9	2	170	151*	-17	13	2	330	277	2	-3	-3	5340	5268
4	5	2	1109	1152	-15	9	2	629	513	4	13	2	305	300*	-1	3	3	4590	4690
-8	5	2	1061	1061	6	9	2	393	413	-16	13	2	177	259*	1	-3	-3	4674	4690
3	5	2	798	808	-14	9	2	231	239*	3	13	2	177	43*	-7	4	3	1770	1799
-7	5	2	3950	3994	5	9	2	277	195	-15	13	2	134	111*	3	4	3	2916	2948
7	-5	-2	3921	3994	-13	9	2	690	686	2	13	2	221	232*	-6	4	3	2137	2135
2	5	2	3886	3993	4	9	2	244	234	-14	13	2	167	229*	6	-4	-3	2101	2135
-2	-5	-2	3799	3993	-12	9	2	1804	1847	1	13	2	225	286*	2	4	3	2169	2201
-6	5	2	3116	3074	3	9	2	1497	1500	-13	13	2	193	136*	-2	-4	-3	2147	2201
6	-5	-2	3062	3074	-11	9	2	185	254*	0	13	2	171	311*	-5	4	3	4042	4081
1	5	2	-115	574	2	9	2	269	333	-12	13	2	235	153*	5	-4	-3	3991	4081
-1	-5	-2	371	574	-10	9	2	-78	95	-1	13	2	158	191*	1	4	3	3098	3100
-5	5	2	263	238	1	9	2	790	820	-11	13	2	495	349	-1	-4	-3	3068	3100
5	-5	-2	495	238	-9	9	2	1657	1612	-2	13	2	759	728	-4	4	3	3102	3101
0	5	2	3804	3758	0	9	2	1030	1081	-10	13	2	458	414	4	-4	-3	3117	3101
0	-5	-2	3790	3758	-8	9	2	818	923	-3	13	2	-192	325	0	4	3	783	420
-4	5	2	5076	5072	-1	9	2	1048	1023	-9	13	2	150	201*	0	-4	-3	794	820
4	-5	-2	5114	5072	-7	9	2	1214	1179	-4	13	2	320	293	-3	4	3	3904	3905
-1	5	2	5234	5261	-2	9	2	1014	974	-8	13	2	481	430	3	-4	-3	3859	3905
1	-5	-2	5214	5261	-6	9	2	2462	2458	-5	13	2	241	153*	-1	4	3	4072	3982
-3	5	2	1463	1501	-3	9	2	2727	2749	-7	13	2	148	229*	1	-4	-3	4008	3982
3	-5	-2	1511	1501	-5	9	2	625	592	-6	13	2	148	146*	-9	5	3	2004	2061
-2	5	2	2086	2054	-4	9	2	-74	297	-17	14	2	185	72*	4	5	3	712	950
2	-5	-2	2034	2054	-18	10	2	194	128*	3	14	2	185	44*	-8	5	3	1805	1933
-11	6	2	692	650	8	10	2	194	162*	-16	14	2	180	307*	3	5	3	3069	3136
5	6	2	373	334	-17	10	2	415	516	2	14	2	180	278*	-7	5	3	1883	1990
-10	6	2	1071	1114	7	10	2	552	436	-15	14	2	330	271	2	5	3	2757	2742
4	6	2	539	502	-16	10	2	171	58*	1	14	2	175	156*	-6	5	3	653	674
-9	6	2	1573	1604	6	10	2	171	116*	-14	14	2	327	355	1	5	3	2039	2031
3	6	2	2118	2191	-15	10	2	164	32*	0	14	2	178	176*	-5	5	3	264	326
-8	6	2	410	487	5	10	2	144	311*	-13	14	2	641	602	5	-5	-3	251	326
2	6	2	534	561	-14	10	2	890	847	-1	14	2	167	167*	0	5	3	670	620
-7	6	2	-62	593	4	10	2	610	483	-12	14	2	409	469	0	-5	-3	642	620
7	-6	-2	-140	593	-13	10	2	300	302	-2	14	2	312	275	-4	5	3	3819	3773
1	6	2	1023	1001	3	10	2	777	775	-11	14	2	222	149*	4	-5	-3	3790	3773
-1	-6	-2	968	1001	-12	10	2	219	363*	-3	14	2	382	264	-1	5	3	4154	4159
-6	6	2	4696	4685	2	10	2	616	651	-10	14	2	525	512	1	-5	-3	4136	4159
6	-6	-2	4637	4685	-11	10	2	1695	1654	-4	14	2	429	489	-3	5	3	3599	3568
0	6	2	4553	4485	1	10	2	1581	1553	-9	14	2	520	499	3	-5	-3	3575	3568
0	-6	-2	4435	4485	-10	10	2	309	316	-5	14	2	-207	195	-2	5	3	3130	3050
-5	6	2	2057	2046	0	10	2	162	165*	-8	14	2	498	437	2	-5	-3	3135	3050
5	-6	-2	2035	2046	-9	10	2	881	875	-6	14	2	347	498	-11	6	3	498	544
-1	6	2	614	976	-1	10	2	458	585	-16	15	2	183	37*	5	6	3	-170	169
1	-6	-2	686	976	-8	10	2	2055	2093	1	15	2	183	146*	-10	6	3	-94	358
-4	6	2	944	1016	-2	10	2	1793	1790	-15	15	2	515	432	4	6	3	767	808
4	-6	-2	970	1016	-7	10	2	512	430	0	15	2	276	288	-9	6	3	731	769
-2	6	2	1210	1272	-3	10	2	1628	1643	-14	15	2	266	257*	3	6	3	1994	1971
2	-6	-2	1222	1272	-6	10	2	-160	310	-1	15	2	175	100*	-8	6	3	1486	1544
-13	7	2	277	181	-4	10	2	781	861	-13	15	2	298	192	2	6	3	1715	1741
6	7	2	268	305	-18	11	2	185	140*	-2	15	2	253	338*	-7	6	3	1337	1419
-12	7	2	371	341	7	11	2	185	23*	-12	15	2	801	760	1	6	3	405	351
5	7	2	498	469	-17	11	2	179	63*	-3	15	2	513	589	-6	6	3	2194	2152
-11	7	2	1483	1488	6	11	2	179	74*	-11	15	2	395	404	0	6	3	1989	1995
4	7	2	1878	1834	-16	11	2	415	384	-4	15	2	166	161*	-5	6	3	1105	1177
-10	7	2	1306	1377	5	11	2	579	462	-10	15	2	164	154*	-1	6	3	401	599
3	7	2	782	828	-15	11	2	358	361	-5	15	2	444	408	-4	6	3	1548	1542
-9	7	2	683	681	4	11	2	166	148*	-9	15	2	700	635	4	-6	-3	1535	1542
2	7	2	1374	1445	-14	11	2	249	143*	-6	15	2	715	757	-2	6	3	1545	1637
-8	7	2	806	848	3	11	2	306	339	-8	15	2	328	302	2	-6	-3	1554	1637
1	7	2	791	785	-13	11	2	1024	973	-7	15	2	257	151*	-13	7	3	509	506
-7	7	2	526	467	2	11	2	1062	1078	-15	16	2	183	60*	6	7	3	580	598
0	7	2	571	624	-12	11	2	376	397	-1	16	2	183	108*	-12	7	3	643	589
-6	7	2	612	624	1	11	2	-213	209	-14	16	2	474	445	5	7	3	-210	287
6	-7	-2	615	624	-11	11	2	547	563	-2	16	2	493	446	-11	7	3	1003	1007
-1	7	2	1173	1157	0	11	2	332	358	-13	16	2	177	33*	4	7	3	1275	1275
1	-7	-2	1161	1197	-10	11	2	1644	1635	-3	16	2	302	137	-10	7	3	1677	1720
-5	7	2	1615	1613	-1	11	2	1832	1766	-12	16	2	175	114*	3	7	3	-149	366
5	-7	-2	1681	1613	-9	11	2	199	274*	-4	16	2	289	225*	-9	7	3	774	932
-2	7	2	3168	3116	-2	11	2	335	239	-11	16	2	833	812	2	7	3	1976	1935

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FC	FC	H	K	L	FO	FC
-8	7	3	1252	1315	-2	11	3	301	361	-9	16	3	174	119*	1	8	4	386	400
1	7	3	813	831	-8	11	3	583	653	-7	16	3	128	152*	-8	8	4	453	532
-7	7	3	592	528	-3	11	3	1154	1084	-1	1	4	1177	1340	0	8	4	1566	1529
0	7	3	1148	1149	-7	11	3	1304	1348	1	-1	-4	1193	1340	-7	8	4	1350	1339
-6	7	3	946	972	-4	11	3	1365	1362	0	1	4	2283	2243	-1	8	4	1197	1135
-1	7	3	-226	77	-6	11	3	161	103*	0	-1	-4	2258	2243	-6	8	4	1094	1168
-5	7	3	1261	1284	-5	11	3	516	544	-3	2	4	3706	3745	-2	8	4	449	476
-2	7	3	2176	2238	-17	12	3	345	365	3	-2	-4	3696	3745	-5	8	4	600	580
-4	7	3	2997	2933	5	12	3	184	93*	1	2	4	375	570	-3	8	4	1251	1234
-3	7	3	949	991	-16	12	3	178	122*	-1	-2	-4	391	570	-17	9	4	186	51*
-15	8	3	459	462	4	12	3	178	201*	-2	2	4	490	464	8	9	4	186	132*
7	8	3	318	224	-15	12	3	164	185*	2	-2	-4	556	464	-16	9	4	179	147*
-14	8	3	461	506	3	12	3	380	396	0	2	4	2274	2323	7	9	4	439	379
6	8	3	768	763	-14	12	3	600	596	0	-2	-4	2251	2323	-15	9	4	393	426
-13	8	3	1111	1147	2	12	3	283	128*	-5	3	4	1403	1455	6	9	4	263	150*
5	8	3	696	678	-13	12	3	165	131*	2	3	4	1699	1667	-14	9	4	306	353
-12	8	3	683	723	1	12	3	462	434	-4	3	4	694	876	5	9	4	303	201
4	8	3	674	737	-12	12	3	592	540	1	3	4	3139	3242	-13	9	4	272	309
-11	8	3	718	668	0	12	3	577	612	-3	3	4	1298	1351	4	9	4	487	510
3	8	3	937	965	-11	12	3	529	713	3	-3	-4	1306	1351	-12	9	4	637	576
-10	8	3	477	426	-1	12	3	161	244*	0	3	4	522	583	3	9	4	693	696
2	8	3	427	563	-10	12	3	290	208	0	-3	-4	520	583	-11	9	4	362	339
-9	8	3	2249	2275	-2	12	3	455	418	-2	3	4	1439	1417	2	9	4	570	629
1	8	3	833	805	-9	12	3	758	783	2	-3	-4	1431	1417	-10	9	4	272	310
-8	8	3	1742	1760	-3	12	3	885	907	-1	3	4	1821	1810	1	9	4	942	1037
0	8	3	2189	2226	-8	12	3	712	680	1	-3	-4	1834	1810	-9	9	4	1045	1072
-7	8	3	1780	1761	-4	12	3	238	27*	-7	4	4	1088	1127	0	9	4	320	336
-1	8	3	1698	1724	-7	12	3	-202	157	3	4	4	1326	1380	-8	9	4	957	959
-6	8	3	2063	2081	-5	12	3	834	780	-6	4	4	-91	409	-1	9	4	330	525
-2	8	3	2107	2054	-17	13	3	345	293	2	4	4	894	975	-7	9	4	679	629
-5	8	3	1020	1017	4	13	3	365	380	-5	4	4	320	446	-2	9	4	1107	1071
-3	8	3	2448	2462	-16	13	3	175	263*	1	4	4	419	500	-6	9	4	545	573
-17	9	3	181	189*	3	13	3	181	158*	-4	4	4	1806	1854	-3	9	4	1244	1263
8	9	3	181	110*	-15	13	3	213	280*	0	4	4	346	306	-5	9	4	1151	1122
-16	9	3	174	120*	2	13	3	395	339	-3	4	4	1219	1293	-4	9	4	800	832
7	9	3	256	404*	-14	13	3	423	346	-1	4	4	1716	1803	-17	10	4	186	176*
-15	9	3	474	420	1	13	3	268	244*	-9	5	4	1172	1263	7	10	4	186	136*
6	9	3	203	155*	-13	13	3	397	365	4	5	4	-75	193	-16	10	4	482	361
-14	9	3	752	814	0	13	3	125	123*	-8	5	4	-196	222	6	10	4	180	96*
5	9	3	330	373	-12	13	3	170	270*	3	5	4	1166	1260	-15	10	4	202	62*
-13	9	3	759	747	-1	13	3	267	344*	-7	5	4	1820	1920	5	10	4	515	537
4	9	3	691	715	-11	13	3	373	288	2	5	4	2104	2122	-14	10	4	345	353
-12	9	3	1035	981	-2	13	3	595	486	-6	5	4	232	178	4	10	4	444	447
3	9	3	1281	1259	-10	13	3	964	993	1	5	4	926	953	-13	10	4	247	211
-11	9	3	802	641	-3	13	3	-161	92	-5	5	4	1654	1635	3	10	4	300	344
2	9	3	786	733	-9	13	3	-192	39	0	5	4	348	470	-12	10	4	245	205
-10	9	3	601	646	-4	13	3	942	880	-4	5	4	2257	2209	2	10	4	300	364
1	9	3	1149	1142	-8	13	3	419	407	-1	5	4	1890	1980	-11	10	4	307	296
-9	9	3	2014	1961	-5	13	3	532	517	-3	5	4	2006	1994	1	10	4	285	475
0	9	3	951	960	-7	13	3	140	279*	-2	5	4	371	197	-10	10	4	428	500
-8	9	3	1753	1768	-6	13	3	109	57*	-11	6	4	295	412	0	10	4	160	26*
-1	9	3	1166	1121	-16	14	3	184	118*	5	6	4	753	774	-9	10	4	-72	278
-7	9	3	2280	2288	2	14	3	319	280	-10	6	4	-80	138	-1	10	4	659	687
-2	9	3	1659	1731	-15	14	3	350	368	4	6	4	825	844	-8	10	4	1489	1489
-6	9	3	1720	1731	1	14	3	144	227*	-9	6	4	-85	164	-2	10	4	1236	1215
-3	9	3	1909	1912	-14	14	3	433	400	3	6	4	790	774	-7	10	4	599	547
-5	9	3	2176	2242	0	14	3	433	350	-8	6	4	1613	1557	-3	10	4	411	478
-4	9	3	1454	1492	-13	14	3	437	356	2	6	4	284	356	-6	10	4	300	252
-17	10	3	151	318*	-1	14	3	438	389	-7	6	4	1137	1163	-4	10	4	860	836
7	10	3	429	428	-12	14	3	312	319	1	6	4	1678	1707	-16	11	4	182	172*
-16	10	3	175	120*	-2	14	3	454	405	-6	6	4	-226	256	5	11	4	132	240*
6	10	3	175	42*	-11	14	3	420	353	0	6	4	701	768	-15	11	4	128	300*
-15	10	3	158	230*	-3	14	3	506	363	-5	6	4	852	860	4	11	4	197	191*
5	10	3	318	279	-10	14	3	461	372	-1	6	4	1363	1344	-14	11	4	171	229*
-14	10	3	857	913	-4	14	3	252	275*	-4	6	4	406	425	3	11	4	326	252
4	10	3	719	768	-9	14	3	740	684	-2	6	4	1359	1421	-13	11	4	481	498
-13	10	3	245	152	-5	14	3	361	312	-13	7	4	601	735	2	11	4	437	397
3	10	3	564	499	-8	14	3	932	912	6	7	4	-179	221	-12	11	4	117	111*
-12	10	3	462	595	-6	14	3	799	836	-12	7	4	-166	44	1	11	4	161	92*
2	10	3	456	430	-16	15	3	187	47*	5	7	4	462	451	-11	11	4	290	270
-11	10	3	1104	1165	1	15	3	187	132*	-11	7	4	114	483*	0	11	4	147	215*
1	10	3	840	828	-15	15	3	395	410	4	7	4	345	342	-10	11	4	289	296
-10	10	3	614	762	0	15	3	183	74*	-10	7	4	1298	1335	-1	11	4	368	346
0	10	3	321	378	-14	15	3	179	231*	3	7	4	-189	474	-9	11	4	622	596
-9	10	3	814	856	-1	15	3	179	208*	-9	7	4	445	462	-2	11	4	247	104*
-1	10	3	1038	1065	-13	15	3	428	453	2	7	4	1479	1450	-8	11	4	313	341
-8	10	3	2168	2135	-2	15	3	366	355	-8	7	4	452	442	-3	11	4	625	573
-2	10	3	2289	2271	-12	15	3	523	458	1	7	4	-229	138	-7	11	4	424	530
-7	10	3	424	324	-3	15	3	459	393	-7	7	4	1172	1164	-4	11	4	1060	994
-3	10	3	1686	1671	-11	15	3	464	368	0	7	4	616	628	-6	11	4	263	335
-6	10	3	564	495	-4	15	3	421	481	-6	7	4	-90	92	-5	11	4	410	391
-4	10	3	666	758	-10	15	3	394	413	-1	7	4	573	635	-16	12	4	183	42*
-17	11	3	182	146*	-5	15	3	446	380	-5	7	4	613	644	4	12	4	355	287
6	11	3	182	185*	-9	15	3	660	600	-2	7	4	-46	517	-15	12	4	178	54*
-16	11	3	355	353	-6	15	3	451	497	-4	7	4	2827	2911	3	12	4	244	200*
5	11	3	340	268	-8	15	3	456	342	-3	7	4	541	631	-14	12	4	451	463
-15	11	3	464	486	-7	15	3	569	495	-15	8	4	543	501	2	12	4	158	257*
4	11	3	171	155*	-15	16	3	187	22*	7	8	4	277	229	-13	12	4	211	215*
-14	11	3	239	188	-1	16	3	187	164*	-14	8	4	279	266	1	12	4	472	379
3	11	3	617	641	-14	16	3	401	408	6	8	4	524	422	-12	12	4	281	89
-13	11	3	619	528	-2	16	3	297	322	-13	8	4	841	843	0	12	4	345	364
2	11	3	830	848	-13	16	3	181	27*	5	8	4	510	525	-11	12	4	372	409
-12	11	3	-111	118	-3	16	3	218	166*	-12	8	4	350	397	-1	12	4	247	270
1	11	3	703	727	-12	16	3	178	36*	4	8	4	174	193*	-10	12	4	113	165*
-11	11	3	168	248*	-4	16	3	178	196*	-11	8	4	567	650	-2	12	4	282	234
0	11	3	139	105*	-11	16	3	398	501	3	8	4	265	251	-9	12	4	218	232*
-10	11	3	1027	1036	-5	16	3	410	491	-10	8	4	151	158*	-3	12	4	132	225*
-1	11	3	1119	1120	-10	16	3	175	222*	2	8	4	256	334	-8	12	4	665	581
-9	11	3	997	914	-6	16	3	175	90*	-9	8	4	1504	1585	-4	12	4	-33	128

ameters, thus introducing only one new parameter, the occupation number p.

The model with Cl(4) instead of Cl(2) at the origin showed the best agreement: $R_w=0{\cdot}111$ against 0·138. This conclusion was also sustained by difference maps. In both cases an occupation number $p\simeq\frac{1}{6}$ was found. The refinement of the best model was continued with coupled anisotropic thermal parameters, and ultimately resulted in $R=0{\cdot}073$, $R_w=0{\cdot}087$ and $p=0{\cdot}133$.

Using Hamilton's R_w-ratio test (1965) and accepting the anisotropic 'disordered' model as zero hypothesis we find that the anisotropic 'ordered' structure can be rejected on a 0·005 significance level: R_w (ratio)$=0{\cdot}097/0{\cdot}087=1{\cdot}115$ while R (1, 1664, 0·005)$=1{\cdot}003$. Notwithstanding this encouraging result, we encountered a number of gross discrepancies between observed and calculated structure factors. Notably the reflexion 012 behaved badly during these refinements, having the values $F_c=13{\cdot}5$ and $F_o=25{\cdot}4$ after the final cycle.

(*b*) *Twinning*

A twinned crystal with (100) as twinning plane produces a diffraction pattern in which reflexions *hkl* and *khl* coincide. Designating F_o' and F_o as observed structure factors for the twinned and untwinned structures respectively, one finds that

$$F_o'^2(hkl)=(1-p)F_o^2(hkl)+pF_o^2(khl)\,, \tag{2}$$

where p is the twinning parameter. Instead of considering positions x, y, z and y, x, z we now add contributions $F_c^2(hkl)$ and $F_c^2(khl)$ according to the equations

$$\begin{aligned}F_o'^2(hkl)&\simeq(1-p)F_c^2(hkl)+pF_c^2(khl)\\ F_o'^2(khl)&\simeq pF_c^2(hkl)+(1-p)F_c^2(khl)\,.\end{aligned} \tag{3}$$

Table 2 (*cont.*)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-7	12	4	266	275	-2	5	5	1303	1351	-8	10	5	1176	1158	0	3	6	195	211*
-5	12	4	735	719	-11	6	5	726	724	-2	10	5	1025	1043	-2	3	6	1306	1324
-16	13	4	348	419	5	6	5	350	358	-7	10	5	268	150	-1	3	6	569	621
3	13	4	186	132*	-10	6	5	456	462	-3	10	5	535	495	-7	4	6	823	858
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H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
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0	1	7	384	529	-11	9	7	246	236*	4	6	8	610	522	-3	5	9	289	262*
-3	2	7	953	913	2	9	7	179	106*	-9	6	8	258	31*	-2	5	9	340	338
1	2	7	180	300	-10	9	7	292	138	3	6	8	165	126*	-7	6	9	135	146*
-2	2	7	-193	162	1	9	7	380	312	-8	6	8	749	660	1	6	9	264	261
0	2	7	557	511	-9	9	7	317	355	2	6	8	297	219	-6	6	9	134	259*
-5	3	7	381	576	0	9	7	319	230	-7	6	8	350	240	0	6	9	221	319*
2	3	7	-225	272	-8	9	7	171	52*	1	6	8	783	741	-5	6	9	492	349
-4	3	7	-148	100	-1	9	7	256	243*	-6	6	8	246	331	-1	6	9	224	167*
1	3	7	950	872	-7	9	7	169	193*	0	6	8	279	277	-4	6	9	290	151*
-3	3	7	693	678	-2	9	7	155	15*	-5	6	8	951	902	-2	6	9	456	343
0	3	7	662	644	-6	9	7	391	362	-1	6	8	-142	331	-3	6	9	277	170*
-2	3	7	163	404*	-3	9	7	395	358	-4	6	8	285	294	-6	7	9	476	370
-1	3	7	363	200	-5	9	7	581	574	-2	6	8	881	840	-2	7	9	185	147*
-7	4	7	239	58*	-4	9	7	302	147	-10	7	8	446	437	-5	7	9	153	191*
3	4	7	180	206*	-12	10	7	185	251*	3	7	8	224	102*	-3	7	9	191	271*
-6	4	7	304	342	2	10	7	185	282*	-9	7	8	431	374	-4	7	9	185	53*
2	4	7	307	325	-11	10	7	182	114*	2	7	8	[illegible]	365					
-5	4	7	156	207*	1	10	7	182	174*	-8	7	8	178	92*					

The twinning parameter is calculated from

$$p=\tfrac{1}{2}-\tfrac{1}{2}\,\frac{F_o'^2(hkl)-F_o'^2(khl)}{F_c^2(hkl)-F_c^2(khl)}\,. \qquad (4)$$

It must be pointed out that equations (3) and (4) are only good approximations if p is small, since the initially calculated structure factors based upon an ordered model are biased by the twinning. From the foregoing treatment of assumed disorder p is expected to be smaller than, say, 0·20.

Using (4) we are now able to determine F_c' for the twinned structure:

$$F_c'(hkl)=[(1-p)F_c^2(hkl)+pF_c^2(khl)]^{1/2}. \qquad (5)$$

Assuming that there are no errors whatsoever in F_o and F_c, the following expression applies

$$F_o-F_o'=F_c-F_c'\,, \qquad (6)$$

and, accordingly, the observed structure factor can be corrected for twinning by adding the difference F_c-F_c' to its observed value. With the new set of F_o values, the refinement of the structure was continued to obtain a better model. Repeating the procedure, p was redetermined using (4) and better values of F_c' and F_o were obtained using (5) and (6). The twinning parameter converged after five cycles to $p=0{\cdot}156$.

According to a procedure explained in the Appendix *all* symmetry-averaged reflexions were corrected for twinning and given new weights. It was now possible to resume the least-squares refinement. Comparison of F_o and F_c after three cycles with isotropic temperature factors gave an indication that the twinning ratio was too high. After a few trials we accepted $p=0{\cdot}141$ as the best value.

The refinement was continued with anisotropic vibrational parameters. It indicated that the strongest 16 reflexions had too high weights. These reflexions were assigned standard errors three times their original values. The refinement converged towards $R=0{\cdot}049$ (omitting non-observed reflexions) and $R_w=0{\cdot}047$.

With two exceptions, shifts were smaller than 0·4 times the standard errors. The shifts for C(3) and C(4) equalled the standard deviations.

Hitherto the choice of space group was not settled. We inspected the centrosymmetric structure with Fe(II) at the origin and average positions for the other atoms. Strictly speaking, we should have redetermined the parameter p, but we accepted the value 0·141, since the centric structure differs slightly from the acentric one and, moreover, p merely showed minor variations during the trials with the various disorder and twinning models. The anisotropic refinement converged for $P\bar{3}$ towards $R=0{\cdot}054$ and $R_w=0{\cdot}066$. It can be seen (Table 6) that the centrosymmetric structure can be rejected on a 0·005 significance level.

As a result of twinning, part of the structure passes into its enantiomorphic form. A determination of the absolute configuration was, therefore, not carried out.

The observed structure factors corrected for a twinning factor of 0·141 and their corresponding calculated

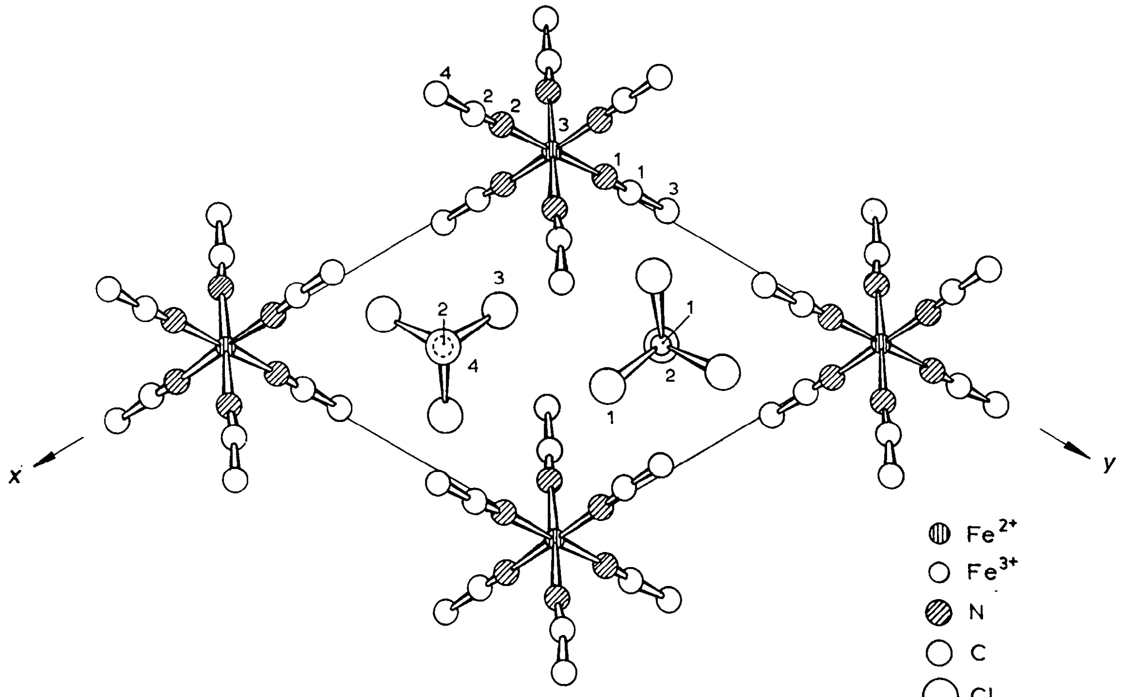

Fig. 2. Projection on (001) plane.

structure factors are listed in Table 2. The positional parameters and their standard deviations are given in Table 3 and the vibrational parameters, U_{ij}, in Table 4.

Table 3. *Atomic parameters* (*in fractions of cell edges*) *and their standard deviations* (Å)

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Fe(1)	$\frac{1}{3}$	0·0	$\frac{2}{3}$	0·0	−0·0420	0·006
Fe(2)	$\frac{2}{3}$	0·0	$\frac{1}{3}$	0·0	0·0442	0·006
Fe(3)	0·0	0·0	0·0	0·0	0·0	0·0
Cl(1)	0·5201	0·004	0·6888	0·003	0·0631	0·006
Cl(2)	$\frac{1}{3}$	0·0	$\frac{2}{3}$	0·0	−0·4011	0·006
Cl(3)	0·4872	0·005	0·3290	0·004	−0·0740	0·006
Cl(4)	$\frac{2}{3}$	0·0	$\frac{1}{3}$	0·0	0·3997	0·007
N(1)	−0·0124	0·010	0·1460	0·010	−0·1843	0·010
N(2)	0·0081	0·012	−0·1452	0·012	0·2289	0·012
C(1)	−0·0103	0·012	0·2258	0·013	−0·2914	0·014
C(2)	0·0219	0·012	−0·2192	0·011	0·3069	0·010
C(3)	−0·0183	0·016	0·3307	0·014	−0·4320	0·015
C(4)	0·0271	0·016	−0·3266	0·013	0·4229	0·012

Table 4. *Vibrational parameters* U_{ij} (Å^2) ($\times 10^3$) *in the temperature factor* $\exp\,[-2\pi^2\sum_{ij} U_{ij}a_i^*a_j^*h_ih_j]$

The estimated standard deviations in digits of the last figure are given in parentheses.

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Fe(1)	47 (1)	47 (1)	39 (2)	47 (1)	0	0
Fe(2)	45 (1)	45 (1)	40 (2)	45 (1)	0	0
Fe(3)	37 (1)	37 (1)	49 (1)	37 (1)	0	0
Cl(1)	43 (1)	91 (2)	73 (2)	71 (3)	−45 (3)	−31 (3)
Cl(2)	86 (3)	86 (3)	30 (3)	86 (3)	0	0
Cl(3)	70 (2)	94 (2)	54 (2)	103 (4)	10 (3)	−11 (3)
Cl(4)	76 (3)	76 (3)	39 (3)	76 (3)	0	0
N(1)	46 (5)	31 (4)	36 (3)	32 (7)	15 (6)	−8 (6)
N(2)	63 (6)	52 (5)	58 (6)	73 (9)	5 (8)	37 (8)
C(1)	25 (4)	54 (6)	80 (8)	10 (8)	−80 (12)	1 (9)
C(2)	41 (5)	46 (5)	40 (5)	52 (8)	46 (7)	9 (7)
C(3)	76 (9)	56 (8)	94 (10)	100 (14)	9 (13)	−12 (14)
C(4)	63 (8)	64 (8)	55 (6)	42 (12)	87 (12)	23 (12)

In the space group $P3$ one atom must have a fixed z parameter. As a result this atom, Fe(3), will have zero standard deviation in its z parameter if full-matrix refinement is applied.

II. *The* Mg–Al *compound*

In the anisotropic refinement of the ordered structure (space group $P3$) disappointingly high indices $R = 0{\cdot}18$ and $R_w = 0{\cdot}21$ were attained. Several models for disorder were examined. The best model is a disordered arrangement with Cl(4) at 0,0,0 and a partial exchange of $Mg(NCCH_3)_6$ and $AlCl_4$ groups. The iteration with anisotropic vibrational parameters for the chlorine atoms resulted in $R = 0{\cdot}150$, $R_w = 0{\cdot}166$ and $p = 0{\cdot}322$. The stumbling block, 012, still showed bad agreement and a number of large B values in the range between 7 and 11 Å^2 were observed for a number of atoms. Nevertheless, the overall agreement had increased substantially. Accepting this model as zero hypothesis, the ordered structure is rejected on a 0·005 significance level.

Since no improvement was obtained with the twinned model as investigated for the Fe–Fe compound, we accepted the disordered model with Cl(4) at 0,0,0 and $p = 0{\cdot}322$. Its geometrical entities are listed in Table 5.

Table 5. *Distances* (Å) *and angles* (°) *in* Me(III)Cl_4 *tetrahedra and* Me(II) $(NCCH_3)_6$ *octahedra*

Estimated standard deviations in digits of the last decimal are given in parentheses. *a*: Fe–Fe compound with twinning parameter $p = 0{\cdot}141$; *b*: the same as *a* but with constraint of equal Fe(3)–N distances; *c*: disordered Mg–Al compound with occupation number $p = 0{\cdot}322$.

Fe(1)/Al(1) tetrahedron	*a*	*b*	*c*
Fe(1)–Cl(1)	2·163 (4)	2·164 (4)	2·15 (2)
Fe(1)–Cl(2)	2·203 (6)	2·228 (7)	2·13 (4)
Cl(1)–Cl(1′)	3·575 (6)	3·584 (7)	3·55 (3)
Cl(1)–Cl(2)	3·517 (6)	3·532 (7)	3·45 (3)
Cl(1)–Fe(1)–Cl(1′)	111·5 (1)	111·8 (1)	111·4 (8)
Cl(2)–Fe(1)–Cl(1)	107·4 (1)	107·1 (1)	107·5 (8)
Fe(2)/Al(2) tetrahedron			
Fe(2)–Cl(3)	2·195 (4)	2·194 (4)	2·14 (1)
Fe(2)–Cl(4)	2·180 (6)	2·153 (7)	2·07 (2)
Cl(3)–Cl(3′)	3·588 (7)	3·578 (7)	3·45 (1)
Cl(3)–Cl(4)	3·568 (6)	3·554 (7)	3·47 (1)
Cl(3)–Fe(2)–Cl(3)	109·7 (2)	109·3 (1)	107·9 (4)
Cl(4)–Fe(2)–Cl(3′)	109·3 (1)	109·7 (1)	111·0 (4)
Fe(3)/Mg octahedron			
Fe(3)–N(1)	2·111 (9)	2·163 (3)	
Fe(3)–N(2)	2·240 (11)		
N(1)–Fe(3)–N(2)	173·5 (5)	180 (ass)	
N(1)–Fe(3)–N(1′)	94·0 (4)	89·7 (1)	
N(2)–Fe(3)–N(2′)	84·9 (4)		
N(1)–Fe(3)–N(2′)	91·2 (4)	90·3 (1)	
N(1)–Fe(3)–N(2″)	89·6 (4)		
N(1)–N(1′)	3·09 (2)	3·050 (5)	3·18 (7)
N(2)–N(2′)	3·02 (2)		2·99 (6)
N(1)–N(2′)	3·11 (1)	3·067 (5)	3·00 (4)
N(1)–N(2″)	3·07 (1)		3·07 (4)

For neither the Fe–Fe nor the Mg–Al compound were indications of macroscopic twinning found. An alternative description is the occurrence of polysynthetic microtwins or twinning domains as described recently by Müller (1971). The domains seem to be very small in the Mg–Al compound resulting in an OD structure (Dornberger-Schiff & Grell-Niemann, 1961). Apparently these domains are larger in the Fe–Fe compound. Nevertheless, the different e.s.d.'s of reflexions $hkil$ and $hh\bar{2h}l$ (see Appendix) might be an indication that the structure of the Fe–Fe compound cannot be accepted as a pure case of twinning.

III. *The* Ni–Ga *compound*

Since reflexions hkl with $h-k=3n$ are much stronger than those with $h-k=3n\pm1$, we first attempted to solve the structure of the subcell $c'=c$, $a'=b'=a/\sqrt{3}$, $\alpha'=\beta'=90°$, $\gamma'=120°$. So far, no solution has been found. The Patterson function indicates that its structure is closely related to that of the Fe–Fe compound.

Discussion of the structures

Relevant interatomic distances and valence angles of the compounds Fe–Fe and Mg–Al together with the estimated standard deviations are listed in Table 5. It must be emphasized that these standard errors are grossly underestimated and do not reflect the uncertainties due to twinning or disorder. A projection of the structure on (001) is given in Fig. 2. Two independent $FeCl_4$ tetrahedra are present at $\frac{1}{3}, \frac{2}{3}, z$ and $\frac{2}{3}, \frac{1}{3}, z$. Each $FeCl_4$ tetrahedron is repeated in the direction [001], giving rise to rows of tetrahedra. An approximate centre of symmetry relating the two tetrahedra exists on the position of Fe(II). Around this Fe(II) ion we notice an octahedron of six $N–C–CH_3$ groups.

A ligand-field spectrum of the compound Mg–Fe (type *A*) was measured by Reedijk & Groeneveld (1968*a*) and interpreted in terms of $FeCl_4^-$ ions in tetrahedral configuration (Balt, 1967). In agreement with this conclusion two quite regular $FeCl_4$ tetrahedra are found in the Fe–Fe structure (see Table 5).

A Mössbauer spectrum (Reedijk & Groeneveld, 1968*a*) has indicated that the Fe–Fe compound contains high-spin Fe(II) and Fe(III) ions. The small isomer shift of Fe(III) points to covalent bonds between Fe(III) and the Cl^- ions. The average Fe–Cl distance (2·18 Å) agrees nicely with the value of 2·19 Å found in the structure of $Fe(NCH)_6(FeCl_4)_2$ (Constant, Daran & Jeannin, 1970).

The average Al–Cl distance (2·13 Å) in the Mg–Al compound agrees very well with the average of Al–Cl distances (2·13 Å) in the $AlCl_4$ tetrahedra of the compound $AlSeCl_7$ (Stork-Blaisse & Romers, 1971).

Inspection of Table 5(*a*) shows that the octahedral coordination of Fe(II) is distorted. We notice three long and three short Fe–N distances (2·24 and 2·11 Å) and unequal N–C distances (Table 7). Far-infrared spectra were, however, interpreted by Reedijk & Groeneveld (1968*b*) in terms of equal Fe–N modes of vibration. Moreover, infrared measurements (Reedijk, Zuur & Groeneveld, 1967) could be explained on the assumption of a regular octahedral coordination of M(II). The measured magnetic susceptibility of the compound Fe–In (type *A*) (Reedijk, 1969) indicates a fairly regular octahedral configuration for the Fe(II) ion, while the small quadrupole splitting in the Mössbauer spectrum (Bancroft, Mays & Prater, 1969) of the Fe–Fe complex suggests that only small deviations from cubic symmetry are present.

We have inspected the presence of a more regular octahedron by carrying out a refinement with constraints: equal Fe(3)–N(1) and Fe(3)–N(2) distances. The atoms N(1) and N(2) kept their separate thermal parameters, but were given positions x, y, z and $\bar{x}, \bar{y}, \bar{z}$. After each cycle, the positional shifts of these atoms were Δx, Δy, Δz and $-\Delta x$, $-\Delta y$, $-\Delta z$ respectively. This refinement resulted in $R_w = 0·048$ and $R = 0·050$. On account of the R_w-ratio test the model with constraints (Table 6) should be rejected.

Table 6. *Numerical data for R_w-ratio tests*

The symbols are explained in Hamilton (1965), significance level $\alpha = 0·005$.

Investigated are twinned structures with $p = 0·141$.

	I	II	III
	Acentric model $P3$	Centric model $P\bar{3}$	Acentric model with equal Fe–N distance
R_w	0·0467	0·0656	0·0482
n	1650	1650	1650
m	87	45	84

$R_w(II)/R_w(I) = 1·405$ $R_w(III)/R_w(I) = 1·032$

$R_{42,\ 1563,\ 0.005} = 1·022$ $R_{3,\ 1563,\ 0.005} = 1·004$

In view of the uncertainties due to twinning, however, we are of the opinion that in this instance no definite choice between the two models can be made. Interatomic distances occurring in the model with constraints are likewise given in Table 5(*b*).

The Fe–N distance of the second model agrees very well with the value 2·16 Å found for the compound $Fe(NCCH_3)_6(FeCl_4)_2$. The longest Fe–N distance (2·24 Å) of the first model is in accord with the Fe–N length (2·25 Å) observed in the complex (HEDTA) FeOFe (HEDTA) $^{2-}$(Lippard, Schugar & Walling, 1967).

Disregarding the carbon atoms, the molecular symmetry of the coordination about Fe(II) is C_3 for the model without constraints and S_6 otherwise. In view of the nearly right angles between the Fe–N bonds, the approximate symmetry of the constrained model is the cubic one O_h.

The relevant distances and angles involving the ligand atoms for models with and without equal Fe(3)–N distances are summarized in Table 7. Although the predicted standard errors for C–C and C–N bonds are about 0·015 Å, we believe that the true errors are at least 0·03 Å, since their positions near pseudo-mirror planes introduce large correlations. In both models the average values for chemically equivalent distances are C–C = 1·51 Å and C–N = 1·10 Å. Constant, Daran & Jeannin (1970) found the value 1·10 Å for the C–N distance in $Fe(NCH)_6(FeCl_4)_2$. In gaseous CH_3CN (Danford & Livingston, 1955) these values are 1·47 (2) and 1·16 (3) Å, respectively. Reedijk, Zuur & Groeneveld (1967) observed a positive shift for the C–N stretching frequency in several M(II) $(NCCH_3)_6$ ions, which is consistent with an increase of the C–N force constant (Purcell & Drago, 1966). According to Purcell (1967) the shortening of the C–N bond is in agreement with the increased force constant for the C–N stretching vibration.

We find non-linear Fe–N–C and N–C–C angles. Judged by statistical criteria, the deviation from linearity is, at least for the second type of angles, not significant, the standard deviations of these angles being about 2°.

Table 7. *Distances* (Å) *and angles* (°) *involving carbon and nitrogen atoms in the* Fe–Fe *compound* ($p=0{\cdot}141$)

Values are given for the model without constraints (*a*) and the model with equal Fe(3)–N distances (*b*).

Columns 2 and 4 refer to average values.

	a		*b*	
N(1)–C(1)	1·13	1·10	1·09	1·10
N(2)–C(2)	1·07		1·11	
C(1)–C(3)	1·54	1·51	1·51	1·51
C(2)–C(4)	1·47		1·51	
Fe(3)–N(1)–C(1)	175	171	173	175
Fe(3)–N(2)–C(2)	167		177	
N(1)–C(1)–C(3)	176	175	176	175
N(2)–C(2)–C(4)	174		174	

The observed deviations may be attributed to packing effects.

It is interesting to note that non-linear C–C–N angles are found in tetracyanoethylene oxide (Stucky, 1971). This author argues that both packing effects and bonding-electron distributions are responsible for the observed distortions.

The space group of $Fe(NCH)_6(FeCl_4)_2$ (Constant, Daran & Jeannin, 1970) is $P\bar{3}$ and the lattice constants are $a=10{\cdot}29$ and $c=6{\cdot}28$ Å. A comparison of Fig. 4 in their article (used is a left-handed coordinate system) with Fig. 2 reveals that the two structures are not isomorphous.

For one thing the ligands and chlorine atoms of the hydrogen cyanide compound are not located near the planes $\{30\bar{3}0\}$. Moreover the relative *z* parameters of the atoms in the two $FeCl_4$ tetrahedra differ considerably from ours.

All calculations were performed on the IBM 360/50 computer of the Central Computing Laboratory of the University of Leiden. We acknowledge the contributions of Mr H. P. Zoetmulder during the beginning of the investigations on the Fe–Fe compound. We appreciate stimulating discussions with Mr R. A. G. de Graaff and Dr J. Reedijk. We thank Mr A. Verhoorn (Geological Institute, University of Leiden) for taking the precession photographs. The investigations were supported with financial aid by the Netherlands Organization for the Advancement of Pure Research (ZWO).

APPENDIX

Using equation (2) we derived the following expressions:

$$F_o(hkl)=\left\{\frac{1-p}{1-2p}F_o'^2(hkl)-\frac{p}{1-2p}F_o'^2(khl)\right\}^{1/2}=A^{1/2} \tag{7}$$

$$\sigma[F_o(hkl)]=\left[\left\{\frac{1-p}{1-2p}\,\sigma[F_o'(hkl)]F_o'(hkl)\right\}^2+\left\{\frac{p}{1-2p}\,\sigma[F_o'(khl)]F_o'(khl)\right\}^2\right]^{1/2}\Big/F_o(hkl)\,. \tag{8}$$

These equations were used for correction of *all* observed reflexions and the assignment of new weights. Due to errors in the measured values of F_o', expression A can assume negative values. A boundary $A\geq 5{\cdot}30$ was used in the program. For $A<5{\cdot}30$ the reflexion was treated as a non-observed one and assigned the value $(|A|)^{1/2}$. The non-observed reflexions were not changed.

Accepting trigonal symmetry and disregarding the small anomalous scattering, mean values and e.s.d.'s for a number of reflexions $hkil$, $ihkl$, $kihl$, $\bar{h}\bar{k}\bar{i}\bar{l}$, $\bar{i}\bar{h}\bar{k}\bar{l}$ and $\bar{k}\bar{i}\bar{h}\bar{l}$ were computed. The e.s.d.'s of these reflexions were compared with the individual standard errors resulting from counting statistics, absorption and the applied polynomial expression. The e.s.d.'s are 1·65 times the standard errors for reflexions with $h\neq k$ and 1·25 times the standard errors for reflexions with $h=k$.

References

ARNDT, U. W. & WILLIS, B. T. M. (1966). *Single Crystal Diffractometry*, p. 37. Cambridge Univ. Press.

BALT, S. (1967). *Rec. Trav. Chim. Pays-Bas*, **86**, 1025.

BANCROFT, G. M., MAYS, M. J. & PRATER, B. E. (1969). *Chem. Phys. Letters*, **4**, 248.

CONSTANT, G., DARAN, J. C. & JEANNIN, Y. (1970). *J. Solid State Chem.* **2**, 421.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.

DANFORD, M. D. & LIVINGSTON, R. L. (1955). *J. Amer. Chem. Soc.* **77**, 2944.

DORNBERGER-SCHIFF, K. & GRELL-NIEMANN, H. (1961). *Acta Cryst.* **14**, 167.

GRAAFF, R. A. G DE (1972). Submitted for publication.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.

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

LIPPARD, S. J., SCHUGAR, H. & WALLING, C. (1967). *Inorg. Chem.* **6**, 1825

MÜLLER, U. (1971). *Acta Cryst.* B**27**, 1997.

PURCELL, K. F. (1967). *J. Amer. Chem. Soc.* **89**, 247.

PURCELL, K. F. & DRAGO, R. S. (1966). *J. Amer. Chem. Soc.* **88**, 919.

REEDIJK, J. (1968). Thesis, Univ. of Leiden.

REEDIJK, J. (1969). *Rec. Trav. Chim. Pays-Bas*, **88**, 86.

REEDIJK, J. & GROENEVELD, W. L. (1968*a*). *Rec. Trav. Chim. Pays-Bas*, **87**, 513.

REEDIJK, J. & GROENEVELD, W. L. (1968*b*). *Rec. Trav. Chim. Pays-Bas*, **87**, 1079.

REEDIJK, J., ZUUR, A. P. & GROENEVELD, W. L. (1967). *Rec. Trav. Chim. Pays-Bas*, **86**, 1127.

STORK-BLAISSE, B. A. & ROMERS, C. (1971). *Acta Cryst.* B**27**, 386.

STUCKY, G. D. (1971). Personal communication.