Acta Cryst. (1956). **9**, 781

The Crystal Structure of Ferric Acetylacetonate*

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(*Received* 19 *August* 1955 *and in revised form* 23 *January* 1956)

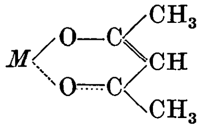
The crystal structure of ferric acetylacetonate, $Fe(C_5H_7O_2)_3$, has been determined by X-ray diffraction. The crystals are orthorhombic with $a = 15{\cdot}471$, $b = 13{\cdot}577$, and $c = 16{\cdot}565$ Å. The unit cell contains eight molecules and the space group is *Pbca*. The trial structure was deduced by use of Harker lines, Patterson projections, and electron-density projections. The approximate atomic coordinates were refined by a bounded projection of a partial three-dimensional Fourier summation, utilizing 775 experimental structure amplitudes. The structure consists of discrete molecules linked together in layers by van der Waals forces. Three acetylacetonate radicals, $(C_5H_7O_2)^{-1}$, surround the central iron atom of each molecule, with the oxygen atoms in octahedral coordination. The three radicals have, within experimental error, a planar configuration. The following interatomic distances were calculated: Fe–O 1·95±0·015 Å, O–C 1·28±0·021 Å, C–C 1·39±0·023 Å, and C–C 1·53±0·023 Å. The assumed octahedral character of the iron atom was confirmed as was the resonance model proposed for the organic radical. The Fe–O distance found is less than the normal ionic distance and explains the non-ionic properties of the compound as well as the relatively large stability of the molecule.

Introduction

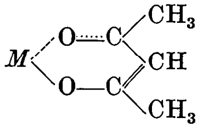
In recent work at the University of Wisconsin on the relative strengths of chelating agents the compound ferric acetylacetonate, $Fe(C_5H_7O_2)_3$, was prepared. Examination of this compound at the University of Michigan revealed a unit cell and space group different from those reported by Astbury (1926). Consequently, a new crystal structure for the compound was determined.

Morgan (1926) has shown that the metallic acetylacetonates cannot be considered as simple metallic salts of an organic acid. They are internal metallic complexes with the central metallic atom so closely associated in the organic radical of the molecule that the metallic atom no longer has ionic properties which are used for its detection in qualitative chemical analysis. In accounting for the exceptional properties of the acetylacetonates of the metals, Morgan assumed that the acetylacetonate radical, $(C_5H_7O_2)^{-1}$, was a chelate group. The addition of a central metal atom, *M*, results in the resonance structure, (I, II), with

(I)



(II)



a plane configuration for the ring system. The relative stability of the metallic acetylacetonates has been associated with a symmetrical arrangement of the chelate groups around the central metallic atom, corresponding in this structure to the arrangement of six oxygen atoms in octahedral coordination around the central iron atom.

Crystallization and morphology

Crystals of ferric acetylacetonate were prepared in the following manner. Washed ferric hydroxide, which had been freshly precipitated, was treated with acetylacetone in slight excess. Ferric acetylacetonate precipitated and was filtered and recrystallized from ether. The color of the crystals is blood-red, and they occur as orthorhombic tabular crystals with {001}, {210}, and {010} predominating.

Astbury (1926) reports the following goniometric measurements: (010):(210) = 60° 22′ and (210):(2$\bar{1}$0) = 59° 16′. The writer's measurements are in excellent agreement with the above: (010):(210) = 60° 22′±2′ and (210):(2$\bar{1}$0) = 59° 16′±5′.

Cleavage is perfect, parallel with {010}, and good, parallel with {210}. Optical data, obtained by immersion methods, are

$$\alpha = 1{\cdot}657,\ \beta = 1{\cdot}666,\ \gamma = 1{\cdot}670;$$
$$\text{sign } (-);\ 2V = 69^\circ \text{ (calc.)}.$$

These values are for room temperature and for red light of approximately 620 mμ. The mean value of the transmitted red band passed by the crystal is 620 mμ, as determined by a wedge interference filter. The orientation of the biaxial indicatrix is α, β, and γ parallel to the c, b, and a axes, respectively, of the orthorhombic system. The plane of the optic axes is (010).

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* Condensed from a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

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Unit cell and space group

In the present work iron radiation was used for the determination of the unit-cell dimensions and for obtaining the intensity data. The lattice constants of ferric acetylacetonate were calculated from zero-level Weissenberg photographs, and Bradley & Jay's (1932) extrapolation procedures were employed. The X-ray camera was calibrated by use of zero-level Weissenberg photographs of a NaCl crystal.

The unit cell dimensions of ferric acetylacetonate are

$$a_0 = 15{\cdot}471,\ b_0 = 13{\cdot}577,\ c_0 = 16{\cdot}565 \pm 0{\cdot}002\ \text{Å}\,.$$

The density determined by the use of a Berman torsion balance, was 1·31 g.cm.$^{-3}$. The calculated density based on eight molecules in the unit cell is 1·34 g.cm.$^{-3}$. Observed extinctions are $\{0kl\}$ for k odd, $\{h0l\}$ for l odd, and $\{hk0\}$ for h odd; from which the space group is unambiguously determined as *Pbca*.

Intensity measurements

The linear absorption coefficient of ferric acetylacetonate is 31 cm.$^{-1}$ and the optimum crystal size, $2/\mu$, is 0·6 mm. A hexagonal crystal approximately 0·5 mm. in size was used to obtain the X-ray intensity data on Weissenberg photographs about the c axis. Reflections from 9,086 planes were recorded on seven levels ($l=6$). The density of the Weissenberg spots was measured by microphotodensitometer methods, and converted to relative intensity through the use of experimental density versus exposure curves. These intensity values were corrected by Lorentz and polarization factors in the usual way. The structure factors obtained from the corrected relative intensity were placed on the absolute scale by comparison with the calculated values of the structure factors obtained in the later stages of analysis.

Determination of the trial structure

The trial structure was deduced by use of Harker lines, Patterson projections, and electron-density projections. The Harker lines were used to find the position of the iron atom. Patterson projections were used to determine the orientation of the Fe–O$_6$ octahedron. Electron-density projections were used to distinguish between the various ways the carbon atoms can be attached to the Fe–O$_6$ octahedron.

From the Harker line syntheses at $(u, \frac{1}{2}b, 0)$, $(0, v, \frac{1}{2}c)$, $(\frac{1}{2}a, 0, w)$, Fig. 1, the trial coordinates of the Fe atoms were determined to be:

$$x=0{\cdot}125\pm\Delta x \text{ or } 0{\cdot}375\pm\Delta x,\ y=0{\cdot}25,\ z=0{\cdot}25\,,$$
$$\text{where } \Delta x = 0{\cdot}018\,.$$

These coordinates are for the octant of the unit cell bounded by the planes at $x=\frac{1}{2}$, $y=\frac{1}{2}$, and $z=\frac{1}{2}$. Equivalent coordinates in other octants can be derived by use of the space-group symmetry elements.

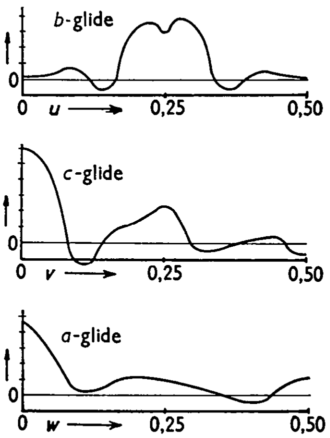


Fig. 1. Harker lines for the b, c, and a glide planes of ferric acetylacetonate.

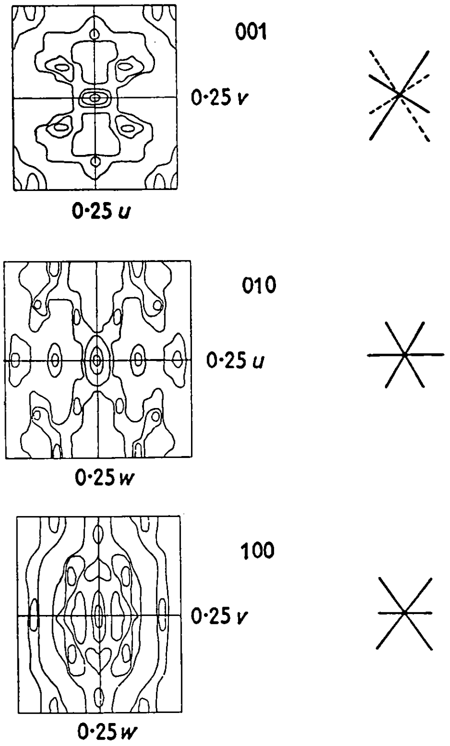


Fig. 2. Patterson projections on the three axial planes and their interpretation in terms of the Fe–O$_6$ octahedron.

The Patterson projections on the three axial planes (Fig. 2) and their interpretation in terms of the Fe–O$_6$ octahedron resulted in a trial orientation of the Fe–O$_6$ octahedron, with one of the trigonal axes of the octahedron parallel with the b axis and one of the twofold axes of the octahedron parallel to the c axis. There are several ways in which the carbon atoms may be joined to the Fe–O$_6$ octahedron. The purpose of the electron-density projection on (001) was to distinguish between the various possibilities. The signs of the coefficients used for the projection of electron density on to (001) were determined by the 'heavy atom' method, with the Fe atom placed at $x = \frac{1}{8}$, $y = \frac{1}{4}$, $z = \frac{1}{4}$. The trial projection of electron density on (001), Fig. 3, showed the way in which the carbon atoms are attached to the Fe–O_6 octahedron. There is a superposition of two molecules.

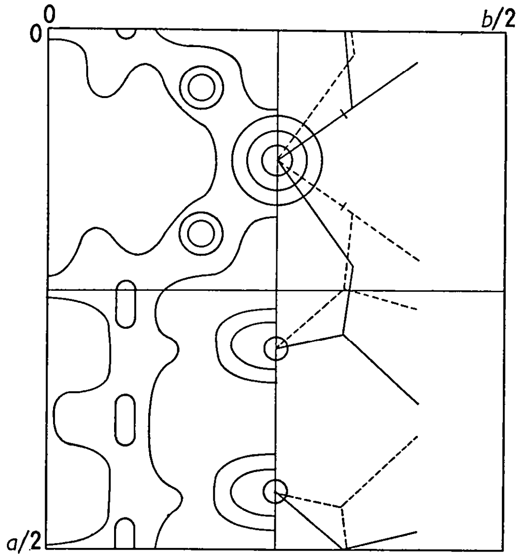


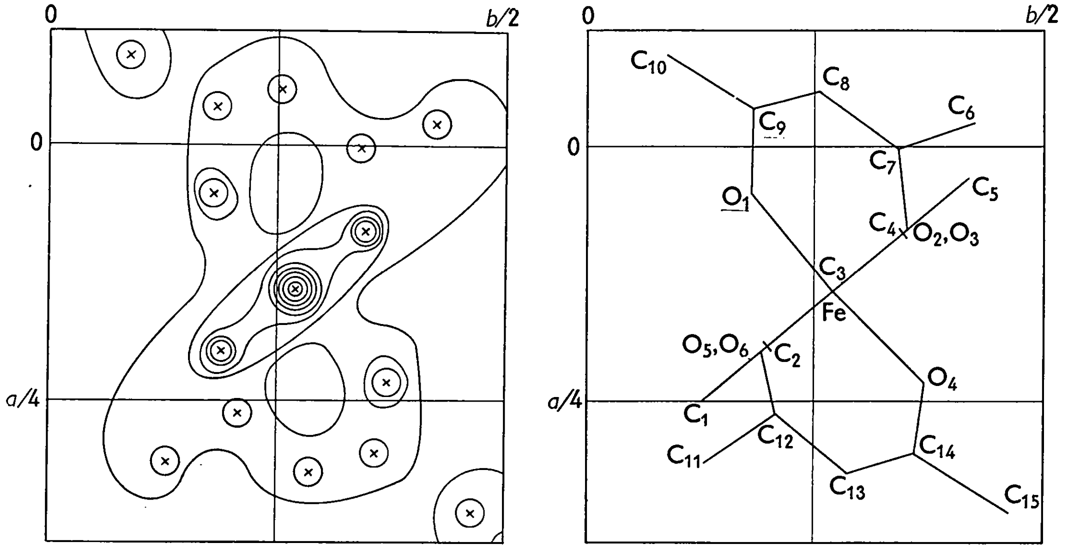
Fig. 3. Trial projection of electron density on (001). Contours drawn at arbitrary intervals. Interpretation in terms of two molecules.

From the trial projection on (001) eight sets of atomic coordinates were derived. Since each set gave identical values for the calculated structure amplitudes, this corresponds to the choice of origin, and the selection of any one set represented the structure upon which the subsequent refinement was based.

Refinement of atomic coordinates

Since the electron-density projection on (001) contains the superposition of *two molecules*, and atomic coordinates could not be accurately assigned, the electron density corresponding to only *one molecule* was used for the refinement of the coordinates. This was done by the partial three-dimensional Fourier summation (Lipson & Cochran, 1953), in which only the zero- and first-level reflections were used in the bounded projection giving 775 terms in the series.

The signs of the coefficients were determined from the calculated structure factors of the approximate structure. Atomic scattering factors were taken from the *Internationale Tabellen* with the iron factor corrected for dispersion of the electrons in the *K* shell (James, 1948), since iron radiation was used. Summations were made on Dr H. J. Grenville-Wells' moving-strip Fourier analyzer, which is an adaptation of Robertson's sorting board (Robertson, 1936). After each summation, changes in atomic parameters were noted and a new set of signs was calculated for the next summation. After nine summations of the series, the iron atom, the oxygen atoms, and thirteen of the fifteen carbon atoms were resolved. Fig. 4(*a*) is the electron-density projection of *one molecule* on to (001). Fig. 4(*b*) is a line diagram of the molecule based on Fig. 4(*a*). Crosses represent the electron-density peaks as determined by the parabola interpolation method of Booth (1948). The atomic coordinates *x* and *y* are



(*a*) (*b*)

Fig. 4. (*a*) Electron density from 0 → ½*c* projected on (001). Contours are drawn at intervals of approximately 0, 5, 10, 15, 20, 25, 30, and 35 e.Å^{-2}. Crosses represent points of maximum electron density. (*b*) Line diagram of a molecule of ferric acetylacetonate as determined from 4(*a*).

Table 1. *Comparison of F_o and F_c*

hkl	F_o	F_c
000	—	1480
200	47	−42
400	18	+17
600	14	+14
800	8	−9
10,0,0	15	−7
12,0,0	20	−22
14,0,0	22	+21
210	295	−277
410	27	+29
610	57	+51
810	4	−6
10,1,0	14	−14
020	384	−435
220	52	+100
420	68	+72
620	66	−52
820	9	+11
10,2,0	17	+15
12,2,0	24	+25
14,2,0	13	−11
230	156	+190
430	73	−110
630	88	−85
830	55	+40
10,3,0	18	+23
040	68	−49
240	22	−36
440	117	−142
640	90	+102
840	53	+35
10,4,0	60	−42
12,4,0	17	−28
250	30	+15
450	93	+113
650	73	+53
850	62	−40
10,5,0	18	−30
12,5,0	12	−10
060	35	+20
260	15	+12
460	71	+40
660	16	−18
860	51	−41
270	12	−9
470	24	−29
670	86	−46
870	18	+14
10,7,0	16	+17
080	4	−3
280	16	−27
480	17	−10
680	0	+3
880	14	+12
290	10	+5
490	38	−30
690	25	+19
890	9	+10
0,10,0	17	+3
2,10,0	10	−12
0,12,0	15	−15
2,12,0	28	+27
211	27	+41
411	68	+88
511	53	+34
611	28	+18
711	2	−2
811	32	−44
14,1,1	16	+12
021	184	+144
121	4	−3
221	18	+19
321	57	+53
421	54	−62
521	20	+20
621	27	−35
821	34	+30
12,2,1	18	+14
131	7	−5
231	57	−84
331	10	+13
431	70	−78
531	46	−43
631	84	+88
12,3,1	24	+33
14,3,1	24	−18
141	6	+8
241	24	−33
341	6	−10
441	85	+116
541	11	+12
641	25	+38
741	34	+39
841	33	−39
151	6	−7
251	6	−4
451	19	+23
651	78	−87
851	30	+28
061	24	−36
261	18	+16
461	97	−102
661	50	+38
861	36	+54
10,6,1	32	+32
271	9	−8
471	16	+10
671	37	+57
871	24	−27
481	32	+36
681	36	−19
10,8,1	21	+17
291	32	+30
491	22	−12
591	7	+4
891	13	+17
10,9,1	15	+19
0,10,1	45	+44
2,10,1	10	−8
3,10,1	9	+6
4,10,1	12	−20
6,10,1	9	+6
10,10,1	8	−9
2,11,1	20	−21
4,11,1	4	+2
2,13,1	18	+16

those shown in Fig. 4(*b*). The *z* coordinates were calculated from measurements on this projection.

Table 1 lists the observed structure factors used in Fig. 4(*a*). The calculated structure factors were obtained from the positions shown in Fig. 4(*b*) and include the effects of an anisotropic temperature factor and the contributions from the hydrogen atoms. An anisotropic temperature factor of the type $\exp\left[-(B_1h^2+B_2k^2+B_3k^2)\right]$ was used with the values of B determined from plots of F_o/F_c versus $\sin^2\theta/\lambda^2$. They are respectively: $B_1 = 0{\cdot}007$, $B_2 = 0{\cdot}012$, and $B_3 = 0{\cdot}009$ Å^{-2}. The hydrogen atoms were placed in their most probable positions with the C–H distance = 1·09 Å.

The accuracy of the determination

It has been found useful to express the over-all agreement of structure factors in terms of the agreement index,

$$R = \Sigma\{|F_o|-|F_c|\}\div\Sigma|F_o|\ ,$$

where $|F_o|$ and $|F_c|$ are the moduli of the observed and calculated structure factors, and the summation is taken over all the reflections. With the positions of the iron, oxygen, and carbon atoms given in Table 3, and the anisotropic temperature factors given above, an agreement index of 0·23 was obtained.

An assessment of the accuracy was made by applying a modification of the treatment described by Cruickshank (1949). The Cruickshank standard deviation of the atomic coordinates is given by

$$\sigma(x) = 2\pi(\Sigma h^2(F_o - F_c)^2)^{\frac{1}{2}}/aVC_{(x)}\,, \qquad (1)$$

where $\sigma(x)$ is the standard deviation in the x coordinates, a is the unit cell edge, V is the volume of the unit cell, and $C_{(x)}$ is the central curvature of the nth atom in the x direction. The central curvature of a particular atom was determined by the method first developed by Costain (1941, see Lipson & Cochran, 1953, p. 279). This equation applies only to atoms that are completely resolved in three dimensions and requires that all of the points of the reciprocal lattice within the limiting sphere be summed. A similar equation can be derived for the calculation of standard deviations of atomic coordinates as determined from a projection on a plane (usually an axial plane), i.e.,

$$\sigma(x) = 2\pi(\Sigma h^2(F_o - F_c)^2)^{\frac{1}{2}}/aAC_{(x)}\,, \qquad (2)$$

where A is the area of the projection plane and the other terms have their usual meanings. This is applicable to atoms that are resolved in projection and requires that all of the points of the reciprocal lattice within the limiting circle be summed.

These equations represent the limiting case of two extremes, i.e., a complete three-dimensional analysis or a projection on an axial plane. For the intermediate case, a partial three-dimensional analysis, when more reciprocal lattice points are necessary than for a projection but the number of reciprocal lattice points used are not sufficient to strictly qualify the analysis as completely three dimensional, the writer suggests that Cruickshank's equation be multiplied by the following factor:

(total number of reciprocal-lattice points theoretically available)÷(actual number of reciprocal-lattice points used in the determination);

thus

$$\sigma(x) = \frac{2\pi(\Sigma h^2(F_o - F_c)^2)^{\frac{1}{2}}}{aVC_{(x)}} \times \frac{\text{total number} \ldots}{\text{actual number} \ldots}\,. \qquad (3)$$

For a three-dimensional analysis when all the available reciprocal-lattice points are used this factor reduces to 1 and Cruickshank's formula is not altered. For a partial three-dimensional analysis this method introduces in the standard deviation equations the contribution of the reciprocal-lattice points used to determine the partial three-dimensional analysis. For a projection the relevant factors in the two equations,

$$\frac{1}{A} \text{ and } \frac{1}{V} \times \frac{\text{total number} \ldots}{\text{actual number} \ldots}$$

would probably tend to be fairly equal and no great error would be introduced by this treatment.

Table 2. *Gaussian probable errors in interatomic distances for ferric acetylacetonate*

(Calculated from formulas described in text)

Interatomic distance	Equation (2) $\Sigma hk0$	Equation (3) $\Sigma hk0$	Equation (3) Σhkl
Fe–O	±0·013 Å	0·016 Å	0·015 Å
O–C	0·018	0·022	0·021
C–C	0·019	0·023	0·023

Table 2 gives the Gaussian probable errors in interatomic distances of ferric acetylacetonate calculated from the above formulas for different conditions.

From columns 2 and 3 in Table 2 it can be seen that the modification of Cruickshank's formula discussed above produces probable errors of the same order of magnitude as Cruickshank's unmodified formula. The modified formula applied to the complete data for ferric acetylacetonate, column 3, gives probable errors of comparable magnitude.

Description of the structure

The atomic coordinates of the iron, oxygen, and carbon atoms are given in Table 3, and the corresponding bond lengths in Table 4. The probable errors in bond lengths derived from the mean are slightly less but of

Table 3. *Fractional atomic coordinates for one molecule*

Atom	x	y	z
Fe	0·136	0·277	0·250
O_1	0·039	0·182	0·250
O_2	0·075	0·350	0·332
O_3	0·075	0·350	0·166
O_4	0·228	0·372	0·250
O_5	0·195	0·200	0·332
O_6	0·195	0·200	0·166
C_1	0·244	0·132	0·051
C_2	0·187	0·210	0·091
C_3	0·136	0·277	0·051
C_4	0·083	0·344	0·091
C_5	0·028	0·420	0·051
C_6	0·979	0·414	0·427
C_7	0·003	0·336	0·370
C_8	0·952	0·254	0·323
C_9	0·972	0·180	0·273
C_{10}	0·911	0·095	0·254
C_{11}	0·300	0·139	0·427
C_{12}	0·266	0·220	0·370
C_{13}	0·322	0·299	0·323
C_{14}	0·297	0·369	0·273
C_{15}	0·354	0·468	0·254

Table 4. *Bond lengths for ferric acetylacetonate*

	C—C (Å)	$\mathrm{C}\overline{\cdots}\mathrm{C}$ (Å)	$\mathrm{C}\overline{\cdots}\mathrm{O}$ (Å)	Fe····O (Å)
Radical 1	1·55	1·38	1·26	1·97
C_1–C_5	1·53	1·39	1·26	1·95
Radical 2	1·53	1·38	1·28	1·96
C_6–C_{10}	1·51	1·40	1·29	1·95
Radical 3	1·54	1·41	1·28	1·94
C_{11}–C_{15}	1·54	1·39	1·29	1·95
Mean	1·53	1·39	1·28	1·95
Probable error	0·012	0·010	0·012	0·012

the same order of magnitude as those calculated by Cruickshank's method.

The light atom interatomic distances agree well with the established values for single bonds between C—C and 50% double-bond character between the C⋯C and the C⋯O.

Within experimental error the acetylacetonate radical is planar. The deviation of an atom from the plane passing through the iron atom and the seven atoms of the organic radical is ±0·011 Å, which is slightly less than the probable error in atomic coordinates, i.e., ±0·02 Å.

The interbond angles for the acetylacetonate radical are shown in Fig. 5, which is an idealized drawing of the organic radical.

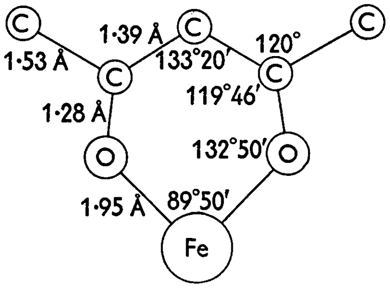


Fig. 5. Interatomic distances and interbond angles in one organic radical of ferric acetylacetonate.

The assumed octahedral character of the iron is confirmed, as is the resonance structure originally proposed by Morgan (1926). The Fe–O distance of 1·95 Å is two-thirds between a pure ionic bond (2·05 Å) and a pure covalent bond (1·90 Å). This corresponds to the non-ionic properties of the compound as well as the relative stability of the molecule.

The crystal structure projected on (001) is shown in Fig. 6(*a*), with the positions of four molecules, related by the *c* glide planes perpendicular to the plane of projection, not shown in order to avoid confusion. The crystal structure projected on (010) is shown in Fig. 6(*b*), with the positions of four molecules, related by the *b* glide planes perpendicular to the plane of the projection, again not shown.

The ferric acetylacetonate crystal structure has discrete molecules linked together in layers by van der Waals forces, with appropriate intermolecular contacts. The closest approach of terminal carbon atoms between molecules in the layers is 3·78 Å for molecules related by the *a* glide, 4·12 Å for molecules related by the *b* glide, and 5·08 Å for molecules related by the *c* glide.

The cleavage properties of the crystal are best explained by reference to Fig. 6(*a*). The perfect cleavage parallel to {010} is attributed to the layer structure of the crystal perpendicular to the *b* axis. Only weak to moderate bonding between molecules occurs perpendicular to {210} and accounts for the cleavage designation of good, parallel with {210}.

The writer wishes to express his gratitude to Dr L. S. Ramsdell for his interest and helpful suggestions throughout the investigation.

Acknowledgment is made to Dr J. H. Norman of the University of Wisconsin for the initial preparation of the compound, and to Mr J. L. Roof of Farnsworth Electronics Co. for the design of the electronic portion of the microphotodensitometer.

The Office of Naval Research supplied funds for the construction of the microphotodensitometer.

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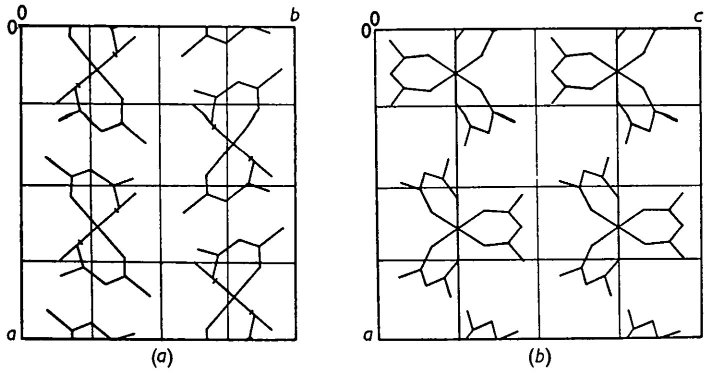

Fig. 6. Structure of ferric acetylacetonate. (*a*) One-half the unit cell 0 → ½*c*, projected on (001); (*b*) one-half the unit cell 0 → ½*b*, projected on (010).