Crystal Structure and Mass Spectrum of μ_3-Oxo-hexakis(μ-trimethylacetato)-trismethanoltri-iron(III) Chloride, a Trinuclear Basic Iron(III) Carboxylate

By **Antony B. Blake** * and **Louis R. Fraser**, Department of Chemistry, The University of Hull, Hull HU6 7RX

The crystal structure of the title compound has been determined by single-crystal *X*-ray diffraction photography, and refined isotropically by the method of least squares to *R* 0·116, based on 552 independent reflections. There are two molecules in a hexagonal unit cell, space group $P6_3$, with a = 10·43(3) and c = 22·79(5) Å. The structure consists of cations $[Fe_3O(piv)_6(MeOH)_3]^+$ (piv = $CMe_3{\cdot}CO_2$) lying on the three-fold axes, with chloride ions on the screw axes. The cation is analogous to that in the chromium(III) and iron(III) basic acetates, except for the rigorous three-fold symmetry and the fact that the central oxygen atom is displaced 0·24 Å from the Fe_3 plane. The mass spectrum is unusual in showing peaks due to ions containing more than three iron atoms, *e.g.* $Fe_4O(piv)_6^+$ which appears in greater abundance than any trinuclear ion.

In the course of a study of the mass spectra of normal and basic pivalates of Mn, Fe, Co, Ni, Cu, and Zn,[1] we observed that crystals prepared from iron(III) chloride and sodium pivalate and recrystallised from chloroform–methanol mixtures gave spectra with peaks at very high mass numbers. Several samples with different crystalline forms were obtained, each of which gave a slightly different spectrum. A typical spectrum showed a moderately strong peak at *m*/*e* 846, to which the formula $Fe_4O(piv)_6^+$ (piv = $CMe_3{\cdot}CO_2$) was assigned, and lesser

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[1] A. B. Blake, K. Compson, L. R. Fraser, and R. B. Moyes, unpublished work.

peaks at *m*/*e* corresponding to the ions $Fe_4O_2(piv)_n^+$ (n = 4—6), $Fe_4O(piv)_7^+$, and $Fe_3O(piv)_n^+$ (n = 3—6). (These assignments are supported by comparisons of peak structure with calculated isotope patterns.) It seemed possible that these ions were derived from a novel tetranuclear complex, *e.g.* $[Fe_4O_2(piv)_8]$, and a crystal-structure analysis was therefore undertaken.

During the analysis it became clear that the crystal studied was in fact a trinuclear complex of a well-established type, with the formula $[Fe_3O(piv)_6(MeOH)_3]Cl$. This crystal was subsequently examined mass-spectrometrically, and found to have a mass spectrum similar to that described, the peak assigned to $Fe_4O(piv)_6^+$ being twice as intense as that due to $Fe_3O(piv)_6^+$. The presence of Cl was confirmed by a precise mass measurement of the peak at *m*/*e* 522, which was shown to be due to $Fe_3O(piv)_3Cl^+$.

EXPERIMENTAL

Preparation and Preliminary Examination.—Equimolar aqueous solutions of iron(III) chloride and sodium pivalate were mixed and the pink precipitate dried in vacuum. Recrystallisation from various solvents gave several crystalline forms belonging to the hexagonal and orthorhombic systems, and some difficulty was found in obtaining a reproducible product. The crystals finally selected for *X*-ray examination were well-formed, orange-yellow, hexagonal plates grown from chloroform–methanol. Unfortunately, not enough of these could be obtained for an elemental analysis, so that when the investigation started the precise contents of the unit cell were unknown.

The unit-cell symmetry and dimensions were determined from zero- and first-level Weissenberg and precession photographs.

Mass spectra were obtained with an A.E.I. MS 902 mass spectrometer at an ionising potential of 70 eV, by use of the direct insertion system.

Crystal Data.—$C_{33}H_{66}ClFe_3O_{16}$, $M = 922{\cdot}0$, hexagonal, $a = 10{\cdot}43 \pm 0{\cdot}03$, $c = 22{\cdot}79 \pm 0{\cdot}05$ Å, $U = 2147 \pm 20$ Å^3, $D_m = 1{\cdot}42$ (flotation), $Z = 2$, $D_c = 1{\cdot}43$, $F(000) = 974$. Cu-K_α radiation, $\lambda = 1{\cdot}542$ Å; $\mu = 94{\cdot}2$ cm^{-1}. Space group $P6_3$, $P6_3/m$, or $P6_322$ from systematic absence: $00l$, l odd.

The accuracy of the hexagonal diffraction symmetry was examined critically and found to be perfect within experimental error. A test for the pyroelectric effect [2] gave a positive result, which (if correct) rules out the centrosymmetric group $P6_3/m$. The structure was successfully solved and refined assuming the non-centric space group $P6_3$ (C_6^6, No. 173).

Data Collection and Reduction.—Multiple-film photographs of the levels 0—3kl were taken by the equi-inclination Weissenberg method, and diffraction intensities were estimated visually by comparison with a calibration strip. Corrections were made for the Lorentz and polarisation effects, and relative scaling of the four levels was accomplished by the logarithmic least-squares method.[3] Of the 789 reflections which had measurable intensity, 552 were unique.

Structure Determination and Refinement.—The three-dimensional sharpened Patterson function indicated the presence of two triangular Fe_3 clusters parallel to (001), with their centres lying either on the 6_3 axis at $0,0,z$ or on the three-fold axis at $\frac{1}{3},\frac{2}{3},z$ ($z = 0$ or $\frac{1}{2}$). Only the second assumption led to a reasonable solution; starting with these positions for iron, successive cycles of phase calculation and Fourier synthesis revealed a large atom at the origin (identified as chlorine), the central oxygen atom, and the carbon and oxygen atoms of the six bridging pivalate ligands, with R 0·22. No terminal ligands were located at this stage, but after a few cycles of isotropic least-squares refinement a difference-Fourier synthesis revealed the three oxygen atom positions and three additional peaks identified as the methanol carbon atoms. (This was the first indication of the presence of methanol in the molecule.)

Isotropic least-squares refinement was continued and convergence was reached at R 0·137. An approximate correction for absorption was then applied to the data, treating the crystal, rather roughly, as a cylinder.[4] After rescaling the individual levels, isotropic refinement was continued, and finally converged at R 0·116. The relatively small number of data (*ca.* 7·7 reflections per isotropic parameter) was felt not to justify further refinement of the structure with anisotropic vibrational parameters. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$, with $w = \{1 + [(F^* - |F_o|)/G^*]^2\}^{-1}$; the values $F^* = 10$, $G^* = 25$ were chosen so that the weighted residuals showed no systematic dependence on intensity.

A three-dimensional difference-Fourier synthesis indicated no inaccuracies in atomic positions, though there were some distortions near the Fe positions, possibly due to anisotropic vibration and/or series termination effects. Although hydrogen atoms contribute nearly 7% of the scattering power in this compound, their location was not practicable, and this undoubtedly detracts from the accuracy of the results.

Atomic scattering factors for carbon, oxygen, and chloride were taken from ref. 5. For iron, the scattering factors of ref. 6 (interpolated for $Fe^{1/3+}$) were used, with anomalous dispersion corrections f', f'' from ref. 5. The difference between Friedel pairs was neglected; the errors resulting from such neglect in polar space groups have been discussed,[7] but in relation to the standard deviations in our final results their effect is not significant.

All calculations were carried out on the Hull University I.C.L. 1905E computer, with programs of ref. 8.

RESULTS AND DISCUSSION

Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21209 (3 pp.,

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[3] A. B. Blake and R. C. Elder, *X*-Ray Crystallographic Intensity Treatment Program for the IBM 709/7090, SHARE distribution No. 3352, IBM Corporation, New York, 1965; A. D. Rae, *Acta Cryst.*, 1965, **19**, 683; A. D. Rae and A. B. Blake, *ibid.*, 1966, **20**, 586.

[4] W. L. Bond, ref. 5, vol. 2, p. 291.

[5] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

[6] R. E. Watson and A. J. Freeman, *Acta Cryst.*, 1961, **14**, 27; A. J. Freeman and R. E. Watson, *ibid.*, p. 231.

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TABLE 1

Atomic fractional co-ordinates ($\times 10^4$) and mean square vibrational amplitudes ($\times 10^3$) *

Atom	x	y	z	U/Å^2
Fe	1554(3)	4823(4)	18(5)	58·4(7)
Cl	0	0	95(8)	54(6)
O(1)	2135(21)	4075(20)	733(10)	48(6)
O(2)	4559(18)	5115(19)	636(8)	39(5)
O(3)	2250(20)	3853(20)	−544(9)	43(5)
O(4)	4678(21)	5217(23)	−643(10)	59(5)
O(5)	−310(17)	2732(16)	113(11)	46(4)
O(6)	$3333\frac{1}{3}$	$6666\frac{2}{3}$	121(15)	35(7)
C(1)	3377(35)	4212(36)	906(16)	57(10)
C(2)	3476(35)	3623(24)	1519(14)	54(9)
C(3)	2322(46)	1893(45)	1376(23)	94(14)
C(4)	5132(39)	3983(40)	1610(15)	63(10)
C(5)	2839(28)	4307(29)	1947(13)	37(7)
C(6)	3453(28)	4416(29)	−815(12)	36(7)
C(7)	3318(30)	3495(29)	−1366(13)	39(7)
C(8)	4871(35)	4067(34)	−1648(15)	55(9)
C(9)	2481(32)	1765(33)	−1371(14)	53(9)
C(10)	2212(52)	3756(53)	−1811(24)	103(16)
C(11)	−1851(26)	2389(26)	−60(13)	41(8)

* In this and subsequent Tables, estimated standard deviations are given in parentheses, in units of the least significant digit.

TABLE 2

Bond lengths (Å) and angles (°) *

(*a*) FeO_6 octahedron and methanol ligand

(i) Distances

Fe–O(1)	2·03(2)	Fe–O(5)	2·08(1)
Fe–O(2^{II})	2·04(2)	Fe–O(6)	1·905(5)
Fe–O(3)	1·98(2)	O(5)–C(11)	1·51(3)
Fe–O(4^{II})	2·05(2)		

(ii) Angles

O(1)–Fe–O(2^{II})	82(1)	O(3)–Fe–O(6)	100(1)
O(1)–Fe–O(3)	94(1)	O(4^{II})–Fe–O(5)	91(1)
O(1)–Fe–O(4^{II})	168(1)	O(4^{II})–Fe–O(6)	102(1)
O(1)–Fe–O(5)	79(1)	O(5)–Fe–O(6)	166(1)
O(1)–Fe–O(6)	88(1)	Fe–O(1)–C(1)	133(2)
O(2^{II})–Fe–O(3)	170(1)	Fe$^{\mathrm{I}}$–O(2)–C(1)	137(2)
O(2^{II})–Fe–O(4^{II})	91(1)	Fe–O(3)–C(6)	128(1)
O(2^{II})–Fe–O(5)	84(1)	Fe$^{\mathrm{I}}$–O(4)–C(6)	123(2)
O(2^{II})–Fe–O(6)	89(1)	Fe–O(5)–C(11)	123(1)
O(3)–Fe–O(4^{II})	91(1)	Fe–O(6)–Fe$^{\mathrm{I}}$	118·5(5)
O(3)–Fe–O(5)	85(1)		

(*b*) Pivalate ligands

(i) Distances above Fe_3 plane		Below Fe_3 plane	
C(1)–C(2)	1·55(5)	C(6)–C(7)	1·54(3)
C(2)–C(3)	1·62(4)	C(7)–C(8)	1·56(4)
C(2)–C(4)	1·59(5)	C(7)–C(9)	1·56(3)
C(2)–C(5)	1·54(4)	C(7)–C(10)	1·66(5)
C(1)–O(1)	1·29(4)	C(6)–O(3)	1·25(3)
C(1)–O(2)	1·27(4)	C(6)–O(4)	1·19(3)

(ii) Angles

C(1)–C(2)–C(3)	96(3)	C(6)–C(7)–C(8)	110(2)
C(1)–C(2)–C(4)	108(3)	C(6)–C(7)–C(9)	123(2)
C(1)–C(2)–C(5)	105(2)	C(6)–C(7)–C(10)	104(2)
C(3)–C(2)–C(4)	114(2)	C(8)–C(7)–C(9)	108(2)
C(3)–C(2)–C(5)	113(3)	C(8)–C(7)–C(10)	111(3)
C(4)–C(2)–C(5)	118(2)	C(9)–C(7)–C(10)	99(2)
O(1)–C(1)–O(2)	119(3)	O(3)–C(6)–O(4)	130(3)
O(1)–C(1)–C(2)	120(3)	O(3)–C(6)–C(7)	111(2)
O(2)–C(1)–C(2)	120(3)	O(4)–C(6)–C(7)	116(2)

* Roman numeral superscripts denote the following equivalent positions relative to the atom at x, y, z:

$$\begin{array}{ll} \mathrm{I} & 1 - y,\ 1 + x - y,\ z \\ \mathrm{II} & y - x,\ 1 - x,\ z \end{array}$$

1 microfiche).* Table 1 lists the fractional co-ordinates and mean square vibrational amplitudes of the atoms, with their estimated standard deviations. Table 2 shows the bond lengths and angles in the trinuclear complex, and Table 3 lists the equations of weighted mean planes passing through certain groups of atoms, the distances of various atoms from these planes, and the angles between the planes. Table 4 gives some distances between non-bonded atoms, including certain distances and angles involving the chloride ion. Figure 1 is a view of the molecule along the *a* axis, with the atomic numbering indicated.

TABLE 3

Equations of planes of best (least-squares) fit to selected groups of atoms, distances of various atoms from planes, and angles between planes

(*a*) Atoms defining planes *

Plane	Group	Atoms
(*A*)	Fe_3	Fe, Fe$^{\mathrm{I}}$, Fe$^{\mathrm{II}}$
(*B*)	FeO_4	Fe, O(1), O(2^{II}), O(3), O(4^{II})
(*C*)	Carboxy	O(1), O(2), C(1)
(*D*)	Carboxy	O(3), O(4), C(6)

(*b*) Equations of planes † in the form $lX + mY + nZ = p$

	10^3l	10^3m	10^3n	10^3p
(*A*)	0	0	1000	−40
(*B*)	806	510	−302	−3170
(*C*)	126	770	626	−3702
(*D*)	−93	970	−226	−2850

(*c*) Distances (Å) of atoms from planes

(*A*): O(5) 0·22, O(6) 0·24, C(11) −0·18
(*B*): Fe 0·10, O(1) −0·52, O(2^{II}) −0·46, O(3) 0·29, O(4^{II}) 0·35
(*C*): Fe −0·25, Fe$^{\mathrm{I}}$ 0·24, C(2) 0·37
(*D*): Fe 1·10, Fe$^{\mathrm{I}}$ 0·90, C(7) −0·57

(*d*) Interplanar angles (°)

(*A*)–(*B*)	107	(*A*)–(*C*)	51

* Atoms defining the planes were given weights proportional to their atomic numbers. † Orthogonal co-ordinates X, Y, Z are related to the fractional co-ordinates of Table 1 as follows: $X = (a\sqrt{3}/2)x$, $Y = by - (a/2)x$, $Z = cz$; l, m, n are the direction cosines of the plane normal, and p is in Å.

TABLE 4

Selected non-bonding distances (Å) and angles (°)

(*a*) Within cation and cation–anion

C(11) $\cdots$ O(2^{II})	3·31(3)	Fe $\cdots$ Fe$^{\mathrm{I}}$	3·274(5)
C(11) $\cdots$ O(4^{II})	3·12(3)	Cl $\cdots$ O(5)	3·02(1)
Cl $\cdots$ O(5)–C(11)	112(1)		
Cl $\cdots$ O(5)–Fe	120(1)		

(*b*) Between cations *

C(11) $\cdots$ C(1^{I})	3·73	C(11) $\cdots$ C(7^{I})	3·79
C(11) $\cdots$ C(6^{I})	3·60	C(11) $\cdots$ C(9^{I})	3·48
C(4^{II}) $\cdots$ C(4^{I})	3·51		

* All distances C $\cdots$ C $< 3·8$ Å are given. In each case the second atom belongs to a molecule in the cell with origin at (−1, −1, 0).

The overall structure is analogous to that found in $[Fe_3O(OAc)_6(H_2O)_3]ClO_4$,[9] $[Cr_3O(OAc)_6(H_2O)_3]Cl,6H_2O$,[10] and $[Mn_3O(OAc)_6(HOAc)(OAc)_{2/2}]_\infty$.[11] The cation has crystallographic point symmetry 3, the iron atoms forming an equilateral triangle of side 3·27 Å, with the central oxygen atom on the three-fold axis but displaced 0·24 Å to one side of the Fe_3 plane, giving Fe–O–Fe angles of

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[9] K. Anzenhofer and J. J. De Boer, *Rec. Trav. chim.*, 1969, **88**, 286.

[10] B. N. Figgis and G. B. Robertson, *Nature*, 1965, **205**, 649; S. C. Chang and G. A. Jeffrey, *Acta Cryst.*, 1970, **B26**, 673.

[11] L. W. Hessel and C. Romers, *Rec. Trav. chim.*, 1969, **88**, 545.

118·5°. The edges of the triangle are bridged by pairs of bidentate pivalate ions, and the sixth position of each iron(III) ion co-ordination sphere is occupied by a methanol oxygen atom.

The Fe–O(central) bonds (1·905 Å) are noticeably shorter than the other Fe–O bonds in the molecule, though the latter do not differ significantly among themselves (mean 2·04 Å, $\pm 2\sigma$); a similar difference was found in the other structures cited.[9-11] The FeO_6 octahedra are rather distorted (O–Fe–O, 79—102°), part of the distortion taking the form of tilting of the Fe–O(central) bonds away from the Fe_3 plane (corresponding to the displacement of the O atom above this plane), and a corresponding outward tilt of the Fe–O-(carboxy) bonds that lie above this plane. These 'upper' carboxy-groups have a symmetrical bridging configuration with a normal O–C–O angle (119°), whereas the 'lower' carboxy-groups are unsymmetrical with a large O–C–O angle (130°) and with the β-carbon atom nearly 0·6 Å out of the OCO plane. The mean FeO_4(carboxy) plane makes an angle of 107° with the Fe_3 plane.

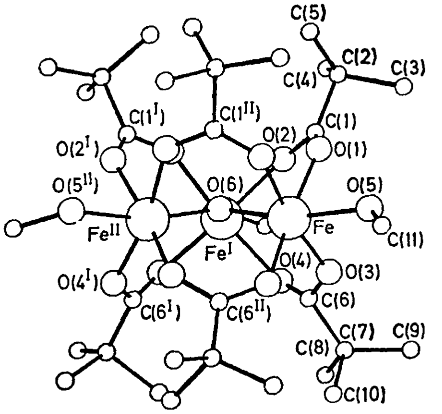

FIGURE 1 A view of the trinuclear cation from a point on the positive *a* axis

The methanol C–O bond is approximately in the Fe_3 plane, and the rather large Fe–O–C angle (123°) is probably due to steric interaction between the methyl group and the adjacent carboxylate oxygen atoms at distances of 3·12 and 3·31 Å.

The packing of the cations and anions in the unit cell is shown in Figure 2. The chloride ions lie almost in the Fe_3 planes, and their distance (3·02 Å) and direction from the methanol oxygen atoms are consistent with hydrogen bonding. The shortest cation–cation contacts are C · · · C *ca.* 3·5 Å between pivalate methyl groups and between pivalate and methanol.

There are two respects in which the structure of the trinuclear cation found in this compound differs significantly from those found in the basic acetates.[9-11] (1) The central oxygen atom is displaced from the Fe_3 plane, and there are substantial deviations of the rest of the molecule from reflection symmetry with respect to this plane, for which we are unable to offer a satisfactory explanation. (2) The complex cation has rigorous three-fold symmetry.

The significance of the latter point is that it may offer the opportunity to resolve a controversy surrounding the interpretation of low-temperature magnetic and thermal data on the trinuclear iron(III) and chromium(III) acetates. These data can readily be interpreted by use of the exchange Hamiltonian appropriate to an isosceles

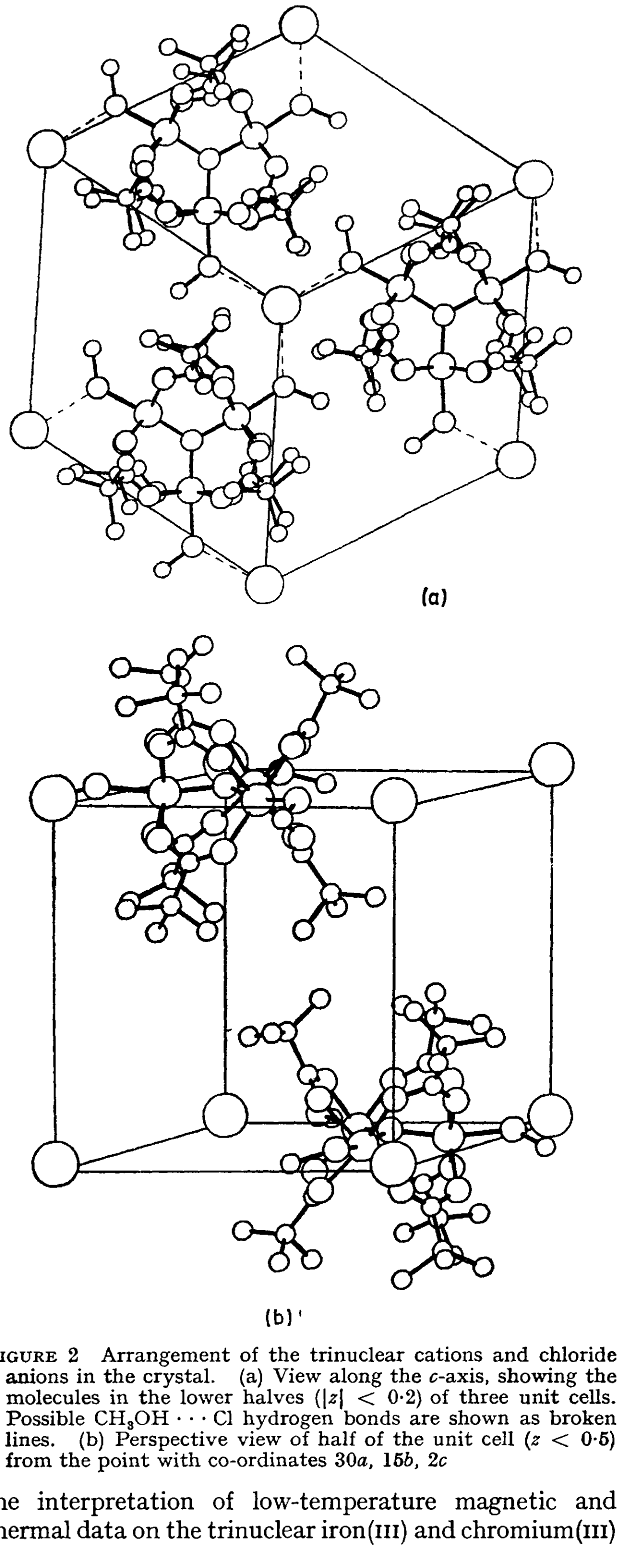

FIGURE 2 Arrangement of the trinuclear cations and chloride anions in the crystal. (a) View along the *c*-axis, showing the molecules in the lower halves ($|z| < 0.2$) of three unit cells. Possible $CH_3OH \cdots Cl$ hydrogen bonds are shown as broken lines. (b) Perspective view of half of the unit cell ($z < 0.5$) from the point with co-ordinates 30*a*, 15*b*, 2*c*

M_3 triangle (in which one interaction differs from the other two by *ca.* 25%), but not one with true three-fold symmetry.[12-14] Unfortunately, although the cation in, *e.g.* $[Cr_3O(OAc)_6(H_2O)_3]Cl,6H_2O$, has no crystallographically imposed symmetry, the Cr_3 triangle is in fact equilateral within the experimental error,[10] and it is not easy to accept that such small deviations from three-fold symmetry as must exist are sufficient to account for the observed magnetic behaviour.[13] [It is possible that more extensive distortion occurs at lower temperatures. Indeed, the chromium(III) complex undergoes a crystalline first-order transition at 211 K (perhaps associated with removal of room-temperature disorder [10]), and it has been suggested that this may be accompanied by distortion of the cations.[14] However, there is as yet no independent evidence for this.] The existence of a complex in which the cation has rigorous three-fold symmetry suggests the possibility of establishing by magnetic measurements whether or not molecular asymmetry is the reason for the unexpected magnetic behaviour of the acetates. It would, of course, be necessary to ascertain that no decrease in symmetry occurred at lower temperatures, but the lack of disorder in $[Fe_3O(piv)_6(MeOH)_3]Cl$ makes this a reasonable expectation.

The mass spectrum of this compound (Table 5) is unusual in that there appears to be present a variety of ions larger than the trinuclear cations present in the crystal. Somewhat similar behaviour has been reported for certain volatile organometallic compounds, *e.g.* $Fe(CO)_5$ [15] and $ArCr(CO)_3$,[16] where it has been shown to be due to ion–molecule reactions in the spectrometer. The fact that one such ion appears in the present case in greater abundance than any ion derived directly from the parent molecule emphasises the hazards of trying to deduce the structure of a solid compound from the compositions of the ions it produces in the mass spectrometer.

TABLE 5

Mass spectrum of $[Fe_3O(piv)_6(MeOH)_3]Cl$ [a] (*m/e* > 480)

m/e [b]	Relative abundance	Assignment
487	74	$Fe_3O(piv)_3^+$
588	33	$Fe_3O(piv)_4^+$
689	21	$Fe_3O(piv)_5^+$
790	48	$Fe_3O(piv)_6^+$
660	37	$Fe_4O_2(piv)_4^+$
761	22	$Fe_4O_2(piv)_5^+$
846	100	$Fe_4O(piv)_6^+$
862	12	$Fe_4O_2(piv)_6^+$
947	29	$Fe_4O(piv)_7^+$
934	12	$Fe_5O_3(piv)_6^+$ [c]
1120	13	$Fe_5O_2(piv)_8^+$
1155	8	$Fe_5O_2(piv)_8Cl^+$
1328	5	$Fe_6O_3(piv)_9Cl^+$
1429	4	$Fe_6O_3(piv)_{10}Cl^+$

[a] piv = $CMe_3{\cdot}CO_2$, $M = 101$. [b] Exact counts were made up to *m/e* 950 using perfluorokerosene as calibrant; slight errors are possible >*m/e* 950, and assignments are less certain. [c] Assignment of this peak confirmed by precise mass measurement.

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