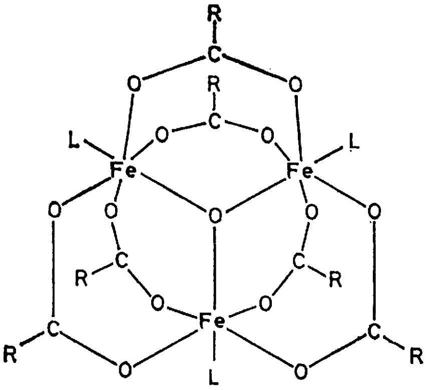
Synthesis, Magnetic Properties, and Mössbauer Spectra of Polynuclear Iron Carboxylates

By **Janet Catterick** and **Peter Thornton**,* Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS
Brian W. Fitzsimmons,* Department of Chemistry, Birkbeck College, London WC1E 7HX

Several carboxylates of iron(II) and iron(III) have been prepared and their magnetic properties and Mössbauer spectra studied. $[Fe_4(OMe)_6(O_2CMe)_6]$, $[Fe_5O(O_2CMe)_{12}][O_2CMe]$, and $[Fe_3(dmf)_3O(O_2CPh)_6][O_2CPh]\cdot dmf$ (dmf = dimethylformamide) are antiferromagnetic but $[Fe_4O(O_2CMe)_{10}]$ is ferromagnetic. $[Fe(O_2CMe)_2]$ and $[Fe(py)_2(O_2CMe)_2]$ are magnetically dilute. The iron(III) compounds show Mössbauer spectra typical of high-spin Fe^{3+} ions, but the spectrum of $[Fe_4O(O_2CMe)_{10}]$ is very asymmetric. The characterizations have been supported by appropriate mass-spectrometric, ebulliometric, and conductimetric studies, and electronic and infrared spectra.

BOTH iron carboxylato-complexes for which complete crystal-structure studies have been reported are salts of the trinuclear cation (1) $[Fe_3L_3O(O_2CR)_6]^+$ ($L = H_2O$, $R = Me$, ref. 1; $L = MeOH$, $R = CMe_3$, ref. 2). Many physical studies have been made of cations of this type, but the older literature [3] contains many other interesting polynuclear formulae and there seems no reason why the trinuclear cluster should be the only one so far identified. This paper describes synthetic and physical studies on various carboxylates which have been obtained from the reaction of $[Fe(CO)_5]$ with acetic or benzoic acids under various conditions and it appears that the structure (1) forms readily in moist air, but if dry or inert atmospheres are maintained other clusters can be formed. The syntheses are summarised in the Scheme (py = pyridine, dmf = dimethylformamide).



(1)

Iron(II) *Compounds*.—Anhydrous iron(II) acetate was prepared by the method of Calderazzo *et al.*,[4] using the reaction of $[Fe(CO)_5]$ with acetic acid and acetic anhydride in dimethylformamide. This gives a purer product than the earlier method [5] involving Soxhlet extraction of metallic iron with acetic acid, in which iron(III) species are easily formed. $[Fe(O_2CMe)_2]$ is easily converted [5] into the bispyridine adduct, but both compounds must be prepared and stored in an atmosphere of dry nitrogen. During the recrystallisation of the yellow $[Fe(py)_2(O_2CMe)_2]$ some green crystals were formed. These may have been $[Fe(py)_4(O_2CMe)_2]$, but they reverted to the 2 : 1 complex while being dried.

TABLE 1

Magnetic susceptibilities (c.g.s. units) and moments (B.M.)

T/K	$10^3\chi_M$	μ	$10^3\chi_M$	μ
	$[Fe(O_2CMe)_2]$		$[Fe(py)_2(O_2CMe)_2]$	
298	11.82	5.31	12.69	5.50
273	12.80	5.29	13.79	5.49
223	15.43	5.24	16.92	5.49
173	19.74	5.22	21.5	5.45
123	27.7	5.15	29.7	5.40
98	32.5	5.05	36.4	5.34
	$[Fe_4O(O_2CMe)_{10}]$		$[Fe_5O(O_2CMe)_{12}]$-$[O_2CMe]$	
298	15.84	6.14	4.72	3.35
273	17.44	6.17	4.88	3.26
223	21.6	6.21	5.29	3.07
173	28.0	6.22	5.95	2.87
123	39.4	6.22	6.65	2.56
98			7.08	2.36
	$[Fe_4(OMe)_6(O_2CMe)_6]$		$[Fe_3(dmf)_3O(O_2CPh)_6]$-$[O_2CPh]\cdot dmf$	
298	10.41	4.98	5.04	3.47
273	11.07	4.91	5.19	3.36
223	12.80	4.78	5.81	3.22
173	15.18	4.58	6.56	3.01
123	19.09	4.33	7.94	2.79
98	21.7	4.13	9.12	2.70

Both compounds have values of magnetic moment appropriate to high-spin iron(II) compounds (Table 1) and have the magnitude and temperature dependence of such axially distorted complexes as $[Fe(isoquinoline)_4I_2]$ and $[Fe(1,10\text{-phenanthroline})_2Br_2]$.[6] Our data for iron(II) acetate differ slightly from those in earlier reports,[4,7] probably reflecting contamination of older samples by iron(III) species. Table 2 lists the diffuse reflectance electronic spectra of both iron(II) compounds and the spectrum of the pyridine complex in chloroform solution. Only one spin-allowed band is expected from an octahedral high-spin d^6 complex, the ${}^5T_{2g}\rightarrow{}^5E_g$ transition. However, even with identical ligands as in $[Fe(H_2O)_6]^{2+}$

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[1] B. N. Figgis and G. B. Robertson, *Nature*, 1965, **205**, 694; K. Anzenhofer and J. J. de Boer, *Rec. Trav. chim.*, 1969, **88**, 286.

[2] A. B. Blake and L. R. Fraser, *J.C.S. Dalton*, 1975, 193.

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[5] H. D. Hardt and W. Möller, *Z. anorg. Chem.*, 1961, **313**, 57.

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[7] A. D. Gonzales, M. A. Navarro, L. A. Oro, and F. Gomez Beltran, *Rev. Acad. Cienc. Exactas. Fis.-Quim. Natur. Zaragoza*, 1972, **27**, 349; *Chem. Abs.*, 1973, **79**, 24478u.

two bands are found,[8] at 8 300 and 10 400 cm^{-1}, and this is attributed to Jahn–Teller splitting of the ^5E_g state. In [Fe(py)$_2$(O$_2$CMe)$_2$] there are inequivalent ligands and the tetragonal splitting of the octahedral states will also contribute to band broadening. Splittings of this order have also been found [9] for adducts of iron(II) halides with heterocyclic bases. The shoulders on the intense allowed band are probably spin-forbidden transitions to components of the ^3P or ^3H free-ion terms.

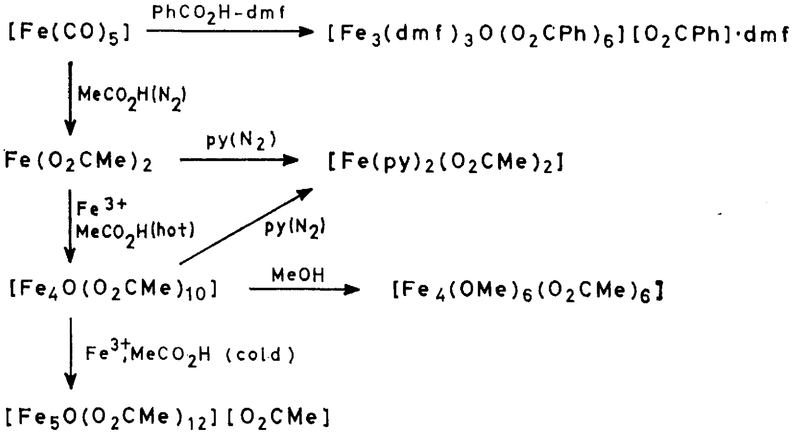
TABLE 2

Electronic spectra (cm^{-1}) of iron(II) complexes

	[Fe(O$_2$CMe)$_2$] (solid)	[Fe(py)$_2$(O$_2$CMe)$_2$] (solid)	[Fe(py)$_2$(O$_2$CMe)$_2$] * (CHCl$_3$)
Bands	7 650	7 420	7 490 (0.18)
	10 900	11 100	11 050 (0.20)
Shoulders	18 900	17 200	18 200
	22 400		

* Molar extinction coefficients (m^{2}mol^{-1}) are given in parentheses.

The electronic spectra and magnetic properties of [Fe(py)$_2$(O$_2$CMe)$_2$] indicate a six-co-ordinate structure analogous to the corresponding nickel [10] and cobalt [11] complexes. As there is no literature report of an electronic spectrum of a high-spin square-pyramidal five-co-ordinate iron(II) complex, it is not possible to decide whether [Fe(O$_2$CMe)$_2$] has the same structure as the uncomplexed copper(II) carboxylates.[12] However, it is curious that this compound is not as strongly antiferromagnetic as other carboxylates of divalent transition metals.[13]



SCHEME

[Fe$_4$O(O$_2$CMe)$_{10}$].—The reaction of [Fe(O$_2$CMe)$_2$] with [Fe$_3$(H$_2$O)$_3$O(O$_2$CMe)$_6$][O$_2$CMe] in acetic acid under nitrogen yields the compound originally formulated [5] as [Fe$_2$(O$_2$CMe)$_5$]. This can be isolated if the solution is filtered hot, but not if the mixture is allowed to cool. The Mössbauer spectrum of this product at 80 K shows one pair of peaks with isomer shift of 0.74 mm s^{-1} relative to Na$_2$[Fe(CN)$_5$(NO)]·2H$_2$O (sodium nitroprusside) and with quadrupole splitting 0.85 mm s^{-1}. These values are typical of high-spin iron(III) compounds [14] and there is no indication of the presence of iron(II). Reformulation of this compound as [Fe$_4$O(O$_2$CMe)$_{10}$] also gives better agreement with the microanalytical data.

The feathery crystals formed by this compound are unsuitable for X-ray studies and assignment of the molecular structure can only be a speculation based on i.r. spectral data. The i.r. spectra in the CO$_2$ stretching region of this and the other iron acetato-complexes studied in this investigation are included in Table 3 with those of sodium acetate [15] and [Fe$_3$(H$_2$O)$_3$O(O$_2$CMe)$_6$]Cl·5H$_2$O.[16] Both the antisymmetric and the symmetric CO$_2$ stretching vibrations are split, suggesting two different types of acetate co-ordination. A similar conclusion was drawn [17] for dimeric vanadium(III) acetate, where the B_1 mode is split into two bands at 1 652 and 1 612 cm^{-1} and the A_1 mode is very broad.

TABLE 3

Carboxyl group stretching frequencies (cm^{-1})

	Anti-symmetric stretch	Symmetric stretch	Separation
Na[O$_2$CMe] ^{a}	1 578	1 414	164
[Fe(O$_2$CMe)$_2$] ^{b}	1 545	1 450	95
[Fe$_4$O(O$_2$CMe)$_{10}$] ^{b}	1 627, 1 560	1 454, 1 380	247 and 106 or 180 and 173
[Fe$_5$O(O$_2$CMe)$_{12}$]-[O$_2$CMe] ^{b}	1 602, 1 518	1 453	149 and 65
[Fe$_4$(OMe)$_6$(O$_2$CMe)$_6$] ^{b}	1 528	1 449	79
[Fe$_3$(H$_2$O)$_3$O(O$_2$CMe)$_6$]Cl·5H$_2$O ^{c}	1 595	1 450	145

^{a} Ref. 15. ^{b} This work. ^{c} Ref. 16.

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[10] J. Catterick and P. Thornton, *J.C.S. Dalton*, 1975, 233.

[11] J. Catterick and P. Thornton, *J.C.S. Dalton*, 1976,1634.

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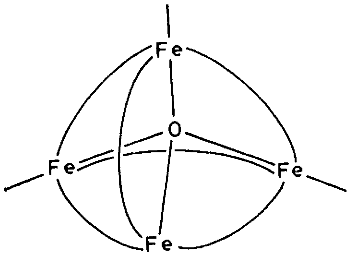
[17] N. N. Greenwood, R. V. Parish, and P. Thornton, *J. Chem. Soc. (A)*, 1966, 320.

However, the interpretation of splitting in the B_1 mode requires care. The dimeric[18] molybdenum(II) carboxylates contain only bridging carboxylate groups but show split B_1 modes;[19] however, the splittings are only 8—18 cm^{-1}, much smaller than those of $[Fe_4O(O_2CMe)_{10}]$ or $[V_2(O_2CMe)_6]$. The vanadium compound retains the splitting in solution, which eliminates crystal effects as a cause of the splitting. $[Fe_4O(O_2CMe)_{10}]$ is insoluble in suitable solvents, but the splitting is large enough to indicate different types of acetate co-ordination. The data can be satisfied by a structure such as (2) which consists of a tetrahedron of iron atoms with the oxygen atom at its centre, a bidentate acetate group located along each edge, and a unidentate acetate group on each iron atom. The $M_4O(O_2CR)_6$ unit from which this proposed structure is derived occurs in cobalt(II) oxopivalate[20] and beryllium[21] and zinc[22] oxoacetates and M_4OX_{10} units also occur in some copper(II) compounds.[23-26]



(2)

The magnetic properties of this compound are the most unusual of those described in this paper, with the magnetic moment being greater than the spin-only value for the sextet ground state of high-spin iron(III) and increasing as the temperature was lowered to 123 K. No measurements were made below this temperature as the high susceptibility caused samples to be pulled to a pole of the magnet even when a very narrow sample tube was used. The results indicate slight ferromagnetic coupling, with a ferromagnetic Weiss constant of −12°. The data can be reproduced on different samples and are not field-dependent. Without *X*-ray confirmation of the proposed structure or data from a greater range of temperatures, it is premature to speculate on the origin of the weak ferromagnetism.

Beside indicating that the compound contains only iron(III) and no iron(II), the Mössbauer spectrum, alone of those of our iron(III) compounds, has a markedly asymmetric appearance, the component at lower isomer shift having about 1.6 times the intensity of its companion. The principal mechanism for relaxation for a ^6S state is spin–spin relaxation, which will only occur between clusters with identical resultant spin S'. For a tetranuclear cluster S' can have integral values 0—10. At room temperature the magnetic moment of 6.14 B.M.* indicates that most of these values are represented in the bulk susceptibility. Thus the probability of a molecule having a neighbour in a state suitable for spin–spin relaxation is relatively low and the relaxation will be slow. The magnetic field then fluctuates and the $\pm\frac{3}{2}\rightarrow\pm\frac{1}{2}$ transitions, which comprise one line of the doublet, will become broad as they have a larger splitting in a magnetic field than the $\pm\frac{1}{2}\rightarrow\pm\frac{1}{2}$ transition, which will be relatively sharper, assuming that the hyperfine field coincides with the z axis of the electric-field gradient, as is normally the case for high-spin iron(III) compounds. This explanation successfully accounted for the temperature-dependent asymmetry in the spectra of some dimeric iron(III) Schiff-base complexes,[27] but the effect is not so striking in our antiferromagnetic iron(III) compounds, where the magnetic interactions are greater and fewer spin states are populated.

The diffuse-reflectance electronic spectrum of $[Fe_4O(O_2CMe)_{10}]$ shows a broad and intense absorption at 13 100 cm^{-1}, which is probably a low-energy charge-transfer band. A possible *d–d* transition occurs near 22 000 cm^{-1} as a shoulder on a much stronger charge-transfer band typical of iron(III) compounds.

$[Fe_5O(O_2CMe)_{12}][O_2CMe]$.—If, instead of being removed by filtration above 80 °C, the green $[Fe_4O(O_2CMe)_{10}]$ is allowed to cool to room temperature in the dry acetic acid used in the Soxhlet extraction, it is transformed into a bright orange solid of stoicheiometry $Fe_5O(O_2CMe)_{13}$. This compound is probably a salt since it can be recovered from water and acetonitrile and is insoluble in chloroform. Its molar conductance in acetonitrile of 43 S cm^2 mol^{-1} at 3×10^{-3} mol dm^{-3} is low for a 1 : 1 electrolyte,[28] even with bulky ions, and suggests some ion pairing together with low mobility for the very large cation. Attempts were made to replace the anionic acetate group by $[BF_4]^-$ or $[PF_6]^-$ by reactions with the appropriate potassium salts in water but no pure products were obtained. The mass spectrum of the complex, which will be discussed in detail below, shows as its highest peak one of m/e value 827, corresponding to $[Fe_5O(O_2CMe)_9]^+$, which points to all the iron atoms being located in the cation. Great care is needed in interpreting mass spectra of this sort of complex since the chloride salt of $[Fe_3(MeOH)_3O(O_2CCMe_3)_6]^+$ gives mass-spectral peaks containing up to six iron atoms.[2]

A possible structure (3) for the pentanuclear $[Fe_5O(O_2CMe)_{12}]^+$ cation consists of a trigonal bipyramid of

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* 1 B.M. ≈ 9.274×10^{-24} A m^2.

[18] F. A. Cotton, *Accounts Chem. Res.*, 1969, **2**, 240.

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[20] A. B. Blake, *Chem. Comm.*, 1966, 569.

[21] G. T. Morgan and W. T. Astbury, *Proc. Roy. Soc.*, 1926, **A112**, 441.

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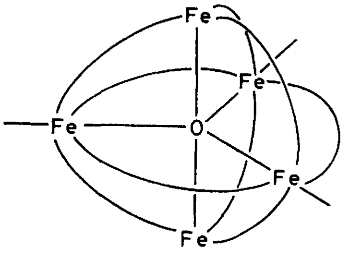
[26] R. Belford, D. E. Fenton, and M. R. Truter, *J.C.S. Dalton*, 1972, 2345.

[27] A. N. Huckley, B. D. Rumbold, G. V. H. Wilson, and K. S. Murray, *J. Chem. Soc.* (*A*), 1970, 2298.

[28] J. F. Coetzee and G. P. Cunningham, *J. Amer. Chem. Soc.*, 1965, **87**, 2529.

iron atoms with the oxygen atom at the centre. Nine acetate groups form bridges along the edges of the bipyramid and a unidentate acetate group is co-ordinated to each equatorial iron atom. The axial iron atoms would thus be tetrahedrally co-ordinated by the central oxygen atom and three bridging acetate groups, and the equatorial iron atoms would be octahedrally co-ordinated by the central oxygen atom, and one unidentate and four bridging acetate groups, while the central oxygen atom would be five-co-ordinate. This proposed structure is only a tentative suggestion based on spectroscopic properties and awaits re-examination in the event of the compound ever being obtained as crystals suitable for an *X*-ray structural examination.



(3)

TABLE 4

Iron-containing lines in the mass spectrum of $[\mathrm{Fe_5O(O_2CMe)_{12}}][\mathrm{O_2CMe}]$

m/e	Ion	Abundance
827	$[\mathrm{Fe_5O(O_2CMe)_9}]^+$	Trace
784	$[\mathrm{Fe_5O_2(O_2CMe)_8}]^+$	Trace
768	$[\mathrm{Fe_5O(O_2CMe)_8}]^+$	Trace
653	$[\mathrm{Fe_4O(O_2CMe)_7}]^+$	25
610	$[\mathrm{Fe_4O_2(O_2CMe)_6}]^+$	1.4
594	$[\mathrm{Fe_4O(O_2CMe)_6}]^+$	23
551	$[\mathrm{Fe_4O_2(O_2CMe)_5}]^+$	4.3
535	$[\mathrm{Fe_4O(O_2CMe)_5}]^+$	0.9
508	$[\mathrm{Fe_4O_3(O_2CMe)_4}]^+$	0.9
492	$[\mathrm{Fe_4O_2(O_2CMe)_4}]^+$	3.2
479	$[\mathrm{Fe_3O(O_2CMe)_5}]^+$	52
449	$[\mathrm{Fe_4O_3(O_2CMe)_3}]^+$	1.7
433	$[\mathrm{Fe_4O_2(O_2CMe)_3}]^+$	3.1
420	$[\mathrm{Fe_3O(O_2CMe)_4}]^+$	57
390	$[\mathrm{Fe_4O_3(O_2CMe)_2}]^+$	2.2
377	$[\mathrm{Fe_3O_2(O_2CMe)_3}]^+$	2.4
374	$[\mathrm{Fe_4O_2(O_2CMe)_2}]^+$	2.4
361	$[\mathrm{Fe_3O(O_2CMe)_3}]^+$	32
331	$[\mathrm{Fe_4O(O_2CMe)}]^+$	1.9
318	$[\mathrm{Fe_3O_2(O_2CMe)_2}]^+$	3.2
305	$[\mathrm{Fe_2O(O_2CMe)_3}]^+$	8.1
302	$[\mathrm{Fe_3O(O_2CMe)_2}]^+$	10
289	$[\mathrm{Fe_2(O_2CMe)_3}]^+$	17
273	$[\mathrm{Fe_2(OCMe)(O_2CMe)_2}]^+$	1.3
259	$[\mathrm{Fe_3O_2(O_2CMe)}]^+$	6.3
230	$[\mathrm{Fe_2(O_2CMe)_2}]^+$	2.9
214	$[\mathrm{Fe_2(OCMe)(O_2CMe)}]^+$	14
174	$[\mathrm{Fe(O_2CMe)_2}]^+$	100
159	$[\mathrm{Fe(O_2C)(O_2CMe)}]^+$	29
155	$[\mathrm{Fe_2(OCMe)}]^+$	21
132	$[\mathrm{Fe(OH)(O_2CMe)}]^+$	18
115	$[\mathrm{Fe(O_2CMe)}]^+$	11
113	$[\mathrm{Fe_2H}]^+$	13
84	$[\mathrm{FeOC}]^+$	13
73	$[\mathrm{FeOH}]^+$	33
56	$[\mathrm{Fe}]^+$	17

The i.r. spectrum of this compound (Table 3) supports the suggested structure by showing a complex group of absorptions in the region of carbonyl-stretching frequencies. There is a little doubt on the assignment of the band at 1 518 cm^{-1}, which is an unusually low frequency for an antisymmetric CO_2 stretching mode, but the band is too intense to be a C–H bending mode, the probable alternative assignment.

Particulars of the mass spectrum of this compound are shown in Table 4. Only ions containing at least one atom of iron are included. The highest peak, at *m/e* 827, corresponding to $[\mathrm{Fe_5O(O_2CMe)_9}]^+$, could be formed by the loss of the three terminal acetate groups of $[\mathrm{Fe_5O(O_2CMe)_{12}}]^+$ as acetoxy radicals. This line was too weak for accurate mass measurement, but this could be done for $[\mathrm{Fe_4O(O_2CMe)_7}]^+$ at *m/e* 653, giving a value of 652.829 992, agreeing with the calculated value of 652.827 763. The base peak is $[\mathrm{Fe(O_2CMe)_2}]^+$ at *m/e* 174, and $[\mathrm{Fe(O_2CMe)_2}]$ fragments are lost in successive steps from heavy ions, as shown in equations (1) and (2), in which asterisks represent transitions for which the appropriate metastable ion was observed.

$$\underset{827}{[\mathrm{Fe_5O(O_2CMe)_9}]^+} \longrightarrow \underset{653}{[\mathrm{Fe_4O(O_2CMe)_7}]^+} \xrightarrow{*} \underset{479}{[\mathrm{Fe_3O(O_2CMe)_5}]^+} \longrightarrow \underset{305}{[\mathrm{Fe_2O(O_2CMe)_3}]^+} \tag{1}$$

$$\underset{594}{[\mathrm{Fe_4O(O_2CMe)_6}]^+} \xrightarrow{*} \underset{420}{[\mathrm{Fe_3O(O_2CMe)_2}]^+} \tag{2}$$

Another fragmentation process involves the loss of acetic anhydride:

$$\underset{653}{[\mathrm{Fe_4O(O_2CMe)_7}]^+} \xrightarrow{*} \underset{551}{[\mathrm{Fe_4O_2(O_2CMe)_5}]^+} \xrightarrow{*} \underset{449}{[\mathrm{Fe_4O_3(O_2CMe)_3}]^+} \tag{3}$$

Peaks due to loss of acetyl or acetoxy radicals could also be distinguished:

$$\underset{827}{[\mathrm{Fe_5O(O_2CMe)_9}]^+} \longrightarrow \underset{784}{[\mathrm{Fe_5O_2(O_2CMe)_8}]^+} \tag{4}$$

$$\underset{827}{[\mathrm{Fe_5O(O_2CMe)_9}]^+} \longrightarrow \underset{768}{[\mathrm{Fe_5O(O_2CMe)_8}]^+} \tag{5}$$

$$\underset{653}{[\mathrm{Fe_4O(O_2CMe)_7}]^+} \longrightarrow \underset{610}{[\mathrm{Fe_4O_2(O_2CMe)_6}]^+} \tag{6}$$

$$\underset{653}{[\mathrm{Fe_4O(O_2CMe)_7}]^+} \longrightarrow \underset{594}{[\mathrm{Fe_4O(O_2CMe)_6}]^+} \tag{7}$$

Some fragmentations involved the loss of more than one of these species:

$$\underset{653}{[\mathrm{Fe_4O(O_2CMe)_7}]^+} \xrightarrow{*} \underset{492}{[\mathrm{Fe_4O_2(O_2CMe)_4}]^+} \tag{8}$$

$$\underset{551}{[\mathrm{Fe_4O_2(O_2CMe)_5}]^+} \xrightarrow{*} \underset{390}{[\mathrm{Fe_4O_3(O_2CMe)_2}]^+} \tag{9}$$

The isotope patterns of some fragment ions were calculated and confirm the assignments. It is curious that of the many acetate complexes studied for iron, cobalt,[11] and nickel,[10] only one is given an ionic formulation and that is the only compound to give us a satisfactory mass spectrum.

The magnetic properties of $[Fe_5O(O_2CMe)_{12}][O_2CMe]$ are given in Table 1. The salt is antiferromagnetic, like the well known salts of the trinuclear $[Fe_3L_3O(O_2CR)_6]^+$ cations.[13] Using the usual spin-coupling methods developed and reviewed [29] by Martin it can be seen that three different exchange integrals are needed to describe the antiferromagnetic interactions. These represent exchange between two equatorial atoms, between two axial atoms, and between one axial and one equatorial atom. We have found this to give 239 different spin-energy levels for the cluster, and there would probably not be a unique fit of J values, especially if the structure is not perfectly regular, so we have not spent further effort on this calculation.

The Mössbauer spectrum of the complex shows a doublet at 0.77 mm s^{-1} relative to sodium nitroprusside with quadrupole splitting 0.65 mm s^{-1}, typical of high-spin iron(III). The diffuse-reflectance electronic spectrum shows a weak *d–d* band, probably the $^6A_{1g}\rightarrow{}^4T_{1g}(G)$ transition at 10 300 cm^{-1} and a shoulder at about 21 600 cm^{-1} on a strong charge-transfer band.

$[Fe_4(OMe)_6(O_2CMe)_6]$.—Despite earlier reports [5,30] that the yellow products formed in the reaction of iron(III) or iron(II) acetates with methanol were not of constant composition, we have found that refluxing $[Fe_4O(O_2CMe)_{10}]$ in methanol under nitrogen gives a yellow precipitate, the reproducible analysis for which leads to its formulation as $Fe_2(OMe)_3(O_2CMe)_3$, provided 2,2-dimethoxypropane is added to prevent hydrolysis. Ebullioscopic molecular-weight determinations in chloroform showed the formulation to be the tetranuclear cluster $[Fe_4(OMe)_6(O_2CMe)_6]$. The magnetic properties of the compound, described in detail below, fit well to spin-exchange theory for a tetrahedron of equivalent iron atoms, in contrast to the rhombus of four iron atoms proposed [31] for $[Fe_4(OMe)_6X_6]$ (X = Cl or Br). A possible structure might be based on a cube having iron atoms and methoxide-oxygen atoms at alternate corners, as in the structures of $[Ni_4(OMe)_4(acac)_4(MeOH)_4]$ [32] and $[Co_4(OMe)_4(acac)_4(O_2CMe)_2]$,[33] but it is hard to predict the complete structure since the i.r. spectrum (Table 3) does not dependably distinguish between unidentate and bridging acetate and methoxide groups.

The magnetic moment of $[Fe_4(OMe)_6(O_2CMe)_6]$ is 4.98 B.M. at 298 K, falling to 4.13 B.M. at 98 K (Table 1). This antiferromagnetic behaviour fits the spin-coupling treatment [29] which gives energy levels $E(S')$ for each spin state S' for the cluster of

$$E(S') = -J[S'(S'+1) - 4S(S+1)] \qquad (10)$$

where S is the spin of one metal ion and J is the isotropic exchange constant, leading to the following equation for the magnetic moment:

$$\mu^2 = 0.5g^2 \frac{\begin{gathered}[15e^{2x} + 105e^{6x} + 336e^{12x} + 720e^{20x} + \\ 1\,155e^{30x} + 1\,365e^{42x} + 1\,400e^{56x} + \\ 1\,224e^{72x} + 855e^{90x} + 385e^{110x}]\end{gathered}}{\begin{gathered}[2 + 15e^{2x} + 35e^{6x} + 56e^{12x} + 72e^{20x} + \\ 77e^{30x} + 65e^{42x} + 50e^{56x} + 65e^{42x} + \\ 50e^{56x} + 34e^{72x} + 19e^{90x} + 7e^{110x}]\end{gathered}} \text{(B.M.)}^2 \qquad (11)$$

where $x = J/kT$. With $g = 2.0$ the best value of J is -4 cm^{-1}. Although this value is much lower than those of dimeric copper(II) carboxylates, it should be remembered that for this compound the difference in energy between the lowest and highest levels is $-110\ J$, compared to $-2\ J$ for the copper dimer.

The Mössbauer spectrum of this compound shows a doublet at 0.76 mm s^{-1} relative to sodium nitroprusside with quadrupole splitting 0.67 mm s^{-1}. Its electronic spectrum shows the weak $^6A_{1g}\rightarrow{}^4T_{1g}(G)$ transition at 10 580 cm^{-1} with shoulders at 14 000 and 21 500 cm^{-1} on a strong charge-transfer band.

$[Fe_3(dmf)_3O(O_2CPh)_6][O_2CPh]\cdot dmf$.—The reaction of iron pentacarbonyl with benzoic acid and benzoic anhydride in dimethylformamide in dry air gives the benzoate salt of another cation of the common type $[Fe_3L_3O(O_2CR)_6]^+$. No doubt this possesses the usual triangular structure (1), although this has not been confirmed crystallographically.

The compound's magnetic moment decreases with temperature (Table 1) but instead of fitting the spin-exchange theory for an equilateral triangle of spins of 5/2 the data satisfy an isosceles triangle with $J_{12} = J_{23} = -17.5$ cm^{-1} and $J_{13} = -30$ cm^{-1}. These results are shown in the Figure. This effect has also been seen [16] in other iron(III) carboxylates with probably regular geometry. In these complexes the carboxylate ions contain bulky alkyl or aryl groups. It is possible that the stacking of the trinuclear cations, perhaps with special locations of the various anions and solvent molecules, may result in inequivalence of the iron atoms which might not be shown in unequal Fe–O distances within the trinuclear cation. The electronic spectrum of this compound is similar to those of our other antiferromagnetic iron(III) compounds in showing a weak band at 10 000 and shoulders at *ca.* 19 100 and 21 700 cm^{-1}.

EXPERIMENTAL

Analyses.—Iron was determined with a Perkin-Elmer 303 atomic absorption spectrophotometer, and carbon, hydrogen, and nitrogen by standard microanalysis in the Alfred Bernhardt laboratories, with extra oxidant added to ensure complete combustion.

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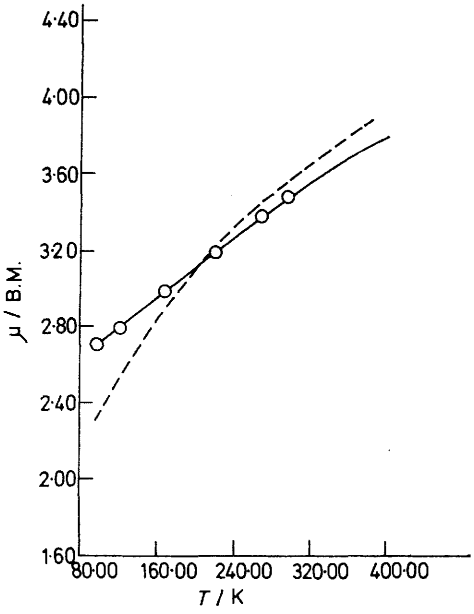
Instrumentation.—Electronic spectra (± 50 cm^{-1}) were obtained on a Beckman DK-2A spectrophotometer with standard diffuse-reflectance attachment. I.r. spectra (± 1 cm^{-1}) were obtained as Nujol or hexachlorobutadiene mulls on a Perkin-Elmer 337 spectrophotometer. Magnetic susceptibility measurements ($\pm 1\%$) were made by the Gouy method using a Newport variable-temperature balance over the range 98—373 K at three different field strengths, with calibration by $Hg[Co(NCS)_4]$.[34] Molecular weights were determined by ebullioscopy in chloroform using a Gallenkamp Semi-Micro Ebulliometer model MW140 with calibration by fluorene. Conductance measurements were made with a Mullard Conductance Bridge type E7566, incorporating a platinum electrode. Mass spectra were recorded by Mr. P. Cook at Queen Mary College using an A.E.I. MS902 instrument with direct insertion. The techniques for obtaining Mössbauer spectra (± 0.04 mm s^{-1}) have been described previously.[35,36]



Temperature dependence of magnetic moment of $[Fe_3(dmf)_3O(O_2CPh)_6][O_2CPh]\cdot dmf$. Circles show experimental data, full curve shows $J_{12} = J_{23} = -17.5$ cm^{-1} and $J_{13} = -30$ cm^{-1}; broken curve shows $J_{12} = J_{23} = J_{13} = -23$ cm^{-1}

Preparations.—*Bisacetatoiron*(II). A method adapted from that of Calderazzo *et al.*[4] was used. Pentacarbonyliron (25.1 g) was filtered into a solution of acetic acid (15 cm^3) and acetic anhydride (2 cm^3) in dimethylformamide (75 cm^3). The bright green solution was heated gently to 80 °C, when there was a moderate evolution of gas. The temperature was gradually increased to 115—120 °C and the solution maintained at this temperature for 60 h during which time it became pale pink. The fine white crystals of $[Fe(O_2CMe)_2]$ were filtered off, washed with benzene, and dried over H_2SO_4 and $CaCl_2$ *in vacuo*. (The other compounds described in this paper were also dried this way unless otherwise stated.) Yield 17.1 g (77%) (Found: C, 27.6; H, 3.6; Fe, 31.0. Calc. for $C_4H_6FeO_4$: C, 27.6; H, 3.45; Fe, 32.1%).

Bisacetatobispyridineiron(II). Bisacetatoiron(II) (2.5 g) was dissolved in hot pyridine (20 cm^3) under nitrogen to give a brown–yellow solution which when set aside gave bright yellow crystals. These were filtered off, recrystallised from pyridine, washed with a little pyridine, and dried *in vacuo* at 90 °C, yield 1.9 g (40%) (Found: C, 50.8; H, 4.80; Fe, 16.6; N, 8.60. Calc. for $C_{14}H_{16}FeN_2O_4$: C, 50.6; H, 4.85; Fe, 16.8; N, 8.45%). Large green crystals were also deposited in the recrystallisation, but these changed to the yellow complex when drying and were probably $[Fe(py)_4(O_2CMe)_2]$.

Decakisacetato-oxotetrairon(III). The method is adapted from that of Hardt and Möller.[5] Bisacetatoiron(II) (3.5 g) and basic iron(III) acetate [37] (4.5 g) were Soxhlet-extracted with acetic acid (90 cm^3) and acetic anhydride (10 cm^3) in a sintered glass thimble under nitrogen for 6 h, with the extract being gently stirred to prevent bumping. Dark green feathery crystals formed during the extraction and were filtered off above 85 °C, washed several times with diethyl ether, and dried; yield 2.7 g (64%, assuming each iron compound contributes an equal number of iron atoms) (Found: C, 29.1; H, 3.55; Fe, 27.2. Calc. for $C_{20}H_{30}Fe_4O_{11}$: C, 28.95; H, 3.65; Fe, 26.9%).

Dodecakisacetato-oxopentairon(III) *acetate*. Bisacetatoiron(II) (2.0 g) and basic iron(III) acetate [37] (5.0 g) were Soxhlet-extracted with acetic acid (90 cm^3) and acetic anhydride (10 cm^3) for 6 h. On cooling to room temperature, the extract deposited a bright orange precipitate which was filtered off, washed several times with diethyl ether, and dried; yield 2.9 g (47% assuming each iron compound contributes an equal number of iron atoms) (Found: C, 29.05; H, 3.75; Fe, 26.35. Calc. for $C_{26}H_{39}Fe_5O_{27}$: C, 29.35; H, 3.70; Fe, 26.30%).

Hexakisacetatohexamethoxotetrairon(III). Decakisacetato-oxotetrairon(III) (1.7 g) was dissolved in a mixture of methanol (25 cm^3) and 2,2-dimethoxypropane (5 cm^3) under nitrogen to give a light brown solution. After the mixture had been heated under reflux for 3 h the pale yellow solid which had been precipitated was filtered off, washed with methanol, and dried; yield 1.25 g (79%) (Found: C, 28.2; H, 4.8; Fe, 29.35%; *M*, 804 ± 60. Calc. for $C_{18}H_{36}Fe_4O_{18}$: H, 28.30; H, 4.75; Fe, 29.25%; *M*, 763).

Hexabenzoatotris(NN-*dimethylformamide*)*oxotri-iron*(III) *benzoate*–NN-*dimethylformamide* (1/1). Pentacarbonyliron (15.0 g) was filtered into a solution of benzoic acid (15.0 g) and benzoic anhydride (4.0 g) in dimethylformamide (50 cm^3). The mixture was heated gradually to 95 °C and then under reflux for 3 d. Most of the solvent was removed under reduced pressure and the solution was left overnight. Brown crystals were deposited, and these were filtered off, washed with benzene, and dried; yield 4.1 g (12%) (Found: C, 55.0; H, 4.85; Fe, 12.7; N, 4.2. Calc. for $C_{61}H_{63}Fe_3N_4O_{19}$: C, 55.35; H, 4.80; Fe, 12.65; N, 4.25%).

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