

Fig. 3. The packing arrangement in the unit cell viewed along *b*.

O(4) forms an intramolecular hydrogen bond with phosphate O(12) (2.62 Å). No such intramolecular interaction is observed in the structure of glucose 1-phosphate (Beevers & Maconochie, 1965). The ring oxygen O(5) accepts a hydrogen bond from the water molecule *W*(5). The distance between the ester oxygen O(6) and the water molecule *W*(3) is 3.03 Å. Since the H atoms of *W*(3) have not been located, it is uncertain whether hydrogen bonding is involved.

The packing arrangement as viewed along *b* is shown in Fig. 3. The molecules (I) and (II), related by the twofold screw axis, are linked to each other through O(1)···O(3) and O(2)···O(11) hydrogen bonds. The O(1)···O(12) interaction connects the molecules along *b*. These three hydrogen bonds arrange the molecules in a spiral fashion around the screw axis. Ba²⁺ ions and water molecules link adjacent columns of G6P molecules.

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Structure of Tricarbonyl(dimethyl 4-methyl-1-oxo-1,3-pentadiene-2,3-dicarboxylate)iron

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Abstract

C₁₃H₁₂FeO₈, *M_r* = 352.08, monoclinic, *P*2₁/*c*, *a* = 7.191 (3), *b* = 21.346 (7), *c* = 10.361 (4) Å, β = 0567-7408/82/041140-05\$01.00

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109.18 (2)°, *V* = 1502 Å³, *Z* = 4, *D_c* = 1.557 g cm⁻³, μ(Mo *K*α) = 10.703 cm⁻¹, *F*(000) = 720. The crystal structure has been determined and refined from 1496 diffractometer data to an *R* value of 0.048. The crystal © 1982 International Union of Crystallography

structure is compared to other known structures containing the vinylketene ligand.

Introduction

In recent years, a number of crystal structures concerning complexes between FeL_3 [$L = \text{CO}$ or $\text{P}(\text{C}_6\text{H}_5)_3$] and the vinylketene ligand ($\eta^3:\eta^1$ -allyl-carbonyl) with various substituents have been published: [(1,2-diphenylvinyl)phenylketene] $\text{Fe}(\text{CO})_3$ (2) (Dettlaf, Behrens & Weiss, 1978), [(2,2-dimethylvinyl)ketene] $\text{Fe}(\text{CO})_3$ (3) (Binger, Cetinkaya & Krüger, 1978), [(2,2-dimethylvinyl)methylketene] $\text{Fe}(\text{CO})_3$ (4) (Newton, Pantaleo, King & Chu, 1979), and (methyl 3-methoxy-4-oxo-1,3-butadiene-2-carboxylate) $\text{Fe}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]$ (5) (Mitsudo, Sasaki, Watanabe & Takegami, 1978). We report here the crystal structure of (dimethyl 4-methyl-1-oxo-1,3-pentadiene-2,3-dicarboxylate) $\text{Fe}(\text{CO})_3$ (1) and compare it to the other known structures in order to discover the influence of the substituents.

Experimental

Suitable single crystals of (1) were obtained by slow evaporation of dichloromethane/pentane solutions at 291 K under an inert atmosphere. A systematic search in reciprocal space using a Philips PW 1100/10 automatic diffractometer and standard software showed that crystals of (1) belong to the monoclinic system, space group $P2_1/c$. The unit-cell parameters were refined at room temperature using $\text{Mo } K\alpha$ radiation and 12 carefully selected reflexions on a Picker automatic diffractometer.

A spherically shaped single crystal of (1) with mean diameter 0.15 ± 0.01 mm was sealed in a Lindemann-glass capillary and mounted on a rotation-free goniometer head (W. Petter, ETH, Zürich, private communication). All quantitative data were obtained using a Picker four-circle diffractometer with graphite-monochromated $\text{Mo } K\alpha$ radiation. Intensity data were collected using the $\theta/2\theta$ scan technique with a scan rate of 2° min^{-1} and a θ scan width ($^\circ$) of $0.85 \pm$ ($\text{Mo } K\alpha_{1,2}$ splitting). Stationary background counts were recorded at each end of the scan for 10 s. The intensities of three reflexions were monitored throughout the data-collection period at intervals of 70 measurements; their values did not vary by more than 2% during the data-collection period. All reflexions within $0.073 < \sin \theta/\lambda < 0.705 \text{ \AA}^{-1}$ were measured.

Structure determination and refinement

All computations were carried out on a Univac 1100 computer. The raw intensity data were converted

to $|F_o|^2$ by application of standard Lorentz and polarization corrections. Absorption corrections were applied (*International Tables for X-ray Crystallography*, 1967). A standard deviation was assigned to each measured intensity using the expression $\sigma(I) = |C + (t_c/t_b)^2(B_1 + B_2) + (pI)^2|^{1/2}$, where C is the scan count, B_1 and B_2 are background counts, t_c and t_b are scan and background times respectively, and p is an empirical coefficient of the net count I (Corfield, Doedens & Ibers, 1967). The factor p was given an initial value of 0.05. A total of 3940 independent reflexions were recorded, but only 1496 had $I > 3\sigma(I)$ and were retained.

The structure was solved using *MULTAN* (Germain, Main & Woolfson, 1970, 1971). All non-hydrogen atoms could be located on the E map of the most probable set.

In all structure factor calculations, the atomic scattering factors used were those tabulated by Moore (1963) using Vand, Eiland & Pepinsky's (1957)

Table 1. Positional parameters and isotropic thermal parameters, and their estimated standard deviations

For non-hydrogen atoms $B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$.

	x	y	z	B_{eq}/B (\AA^2)
Fe	0.0365 (2)	0.32289 (4)	0.1876 (1)	2.80 (2)
O(1)	0.0305 (9)	0.3204 (2)	-0.0993 (5)	4.9 (2)
O(9)	-0.0965 (7)	0.4603 (2)	0.3135 (5)	3.0 (2)
O(10)	0.1382 (7)	0.5179 (2)	0.2770 (5)	2.5 (2)
O(13)	-0.2395 (7)	0.4872 (2)	0.0083 (5)	2.7 (2)
O(14)	-0.3370 (7)	0.3978 (2)	-0.1079 (5)	3.7 (2)
O(17)	-0.0346 (12)	0.3271 (3)	0.4521 (7)	5.9 (3)
O(19)	-0.3121 (10)	0.2448 (3)	0.0736 (8)	5.2 (3)
O(21)	0.3294 (11)	0.2242 (3)	0.2407 (8)	2.9 (2)
C(2)	0.029 (1)	0.3415 (3)	0.0065 (7)	3.6 (6)
C(3)	-0.025 (1)	0.3999 (3)	0.0570 (7)	3.3 (1)
C(4)	0.103 (1)	0.4177 (3)	0.1872 (7)	4.0 (2)
C(5)	0.288 (1)	0.3888 (3)	0.2442 (8)	2.5 (2)
C(6)	0.396 (2)	0.3986 (5)	0.3963 (12)	3.5 (6)
C(7)	0.424 (1)	0.3784 (4)	0.1643 (12)	3.7 (1)
C(8)	0.032 (1)	0.4671 (3)	0.2657 (7)	4.6 (2)
C(11)	0.091 (1)	0.5705 (4)	0.3512 (10)	4.5 (2)
C(12)	-0.211 (1)	0.4332 (3)	-0.0141 (6)	7.2 (2)
C(15)	-0.520 (1)	0.4288 (4)	-0.1900 (10)	4.2 (2)
C(16)	-0.008 (1)	0.3277 (3)	0.3512 (8)	7.4 (2)
C(18)	-0.179 (1)	0.2756 (4)	0.1176 (9)	4.4 (2)
C(20)	0.213 (1)	0.2621 (3)	0.2234 (9)	7.7 (2)
H(C6)	0.47 (1)	0.431 (5)	0.405 (10)	5
H''C(6)	0.46 (2)	0.365 (5)	0.428 (10)	5
H''C(6)	0.30 (2)	0.406 (4)	0.463 (10)	5
HC(7)	0.36 (2)	0.381 (5)	0.061 (11)	5
H''C(7)	0.49 (1)	0.339 (5)	0.182 (9)	5
H''C(7)	0.50 (2)	0.411 (5)	0.173 (10)	5
HC(11)	-0.03 (2)	0.575 (5)	0.326 (11)	5
H''C(11)	0.17 (1)	0.603 (5)	0.336 (10)	5
H''C(11)	0.14 (2)	0.559 (5)	0.438 (11)	5
HC(15)	-0.49 (1)	0.461 (5)	-0.259 (10)	5
H''C(15)	-0.59 (1)	0.449 (4)	-0.124 (10)	5
H''C(15)	-0.59 (1)	0.399 (5)	-0.229 (10)	5

modifications. The effects of anomalous dispersion were included for the Fe atoms (*International Tables for X-ray Crystallography*, 1962).

A difference map computed at the end of isotropic refinement revealed electron density concentrations close to the calculated positions for H atoms, which were then introduced in calculations with isotropic temperature factors of 5 \AA^2 .

Atomic coordinates and the individual anisotropic thermal parameters for all non-hydrogen atoms were refined by full-matrix least squares using the program *SFLS-5* (Prewitt, 1966). In all least-squares calculations the function minimized was $\sum w(|F_o| - |F_c|)^2$, where the weight w was taken as $1/\sigma^2(F_o)$. A p value of 0.08 was used in the last cycles of refinement.

The refinement converged to $R_1 = \sum (|F_o| - |F_c|)/\sum |F_o|$ of 0.048 and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ of 0.064. The standard deviation of a unit-weight observation is 1.13.

A final difference map showed no maxima greater than 0.25 e \AA^{-3} .

The positional and thermal parameters of all atoms appear in Table 1.*

Description of the crystal structure

The structure consists of discrete molecules linked only by van der Waals contacts and hydrogen bonds. Fig. 1 shows an *ORTEP* plot (Johnson, 1965) of the complex, without H atoms; ellipsoids are scaled to enclose 50% of the electronic density. Table 2 gives selected bond distances and angles and Table 3 selected mean planes. Table 4 gives selected geometrical data for other known structures containing the vinylketene moiety.

* Lists of structure factors, anisotropic thermal parameters, and packing distances less than 3.20 \AA have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36525 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

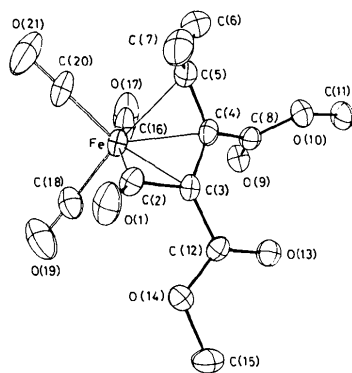


Fig. 1. *ORTEP* drawing of molecule (1) with the labelling scheme used. H atoms are omitted for clarity.

The $Fe(CO)_3$ trigonal pyramid is covered by the vinylketene unit which can be represented by a resonance hybrid between the diene (*A*) and the $2\sigma-\pi$ (*B*) complexes.

Table 2. Selected bond distances (\AA) and angles ($^\circ$) with their estimated standard deviations

Fe—C(2)	1.902 (7)	O(1)—C(2)—C(3)	137.8 (7)
Fe—C(3)	2.082 (6)	C(2)—C(3)—C(4)	114.0 (6)
Fe—C(4)	2.079 (5)	C(2)—C(3)—C(12)	122.4 (6)
Fe—C(5)	2.213 (7)	C(3)—C(4)—C(5)	120.8 (6)
Fe—C(16)	1.827 (9)	C(3)—C(4)—C(8)	118.0 (6)
Fe—C(18)	1.792 (8)	C(4)—C(5)—C(6)	117.7 (7)
Fe—C(20)	1.768 (8)	C(4)—C(5)—C(7)	122.3 (7)
O(1)—C(2)	1.187 (9)	C(4)—C(3)—C(12)	123.0 (6)
C(2)—C(3)	1.454 (4)	C(1)—C(4)—C(8)	121.1 (6)
C(3)—C(4)	1.411 (8)	C(3)—C(12)—O(13)	121.1 (6)
C(4)—C(5)	1.408 (9)	C(3)—C(12)—O(14)	112.3 (6)
C(3)—C(12)	1.483 (8)	O(13)—C(12)—O(14)	124.7 (6)
C(12)—O(13)	1.207 (7)	C(12)—O(14)—C(15)	115.7 (6)
C(12)—O(14)	1.324 (7)	C(4)—C(8)—O(9)	125.5 (6)
O(14)—C(15)	1.466 (9)	C(4)—C(8)—O(10)	109.4 (5)
C(4)—C(8)	1.52 (1)	O(9)—C(8)—O(10)	125.0 (6)
C(8)—O(9)	1.19 (1)	C(8)—O(10)—C(11)	116.8 (6)
C(8)—O(10)	1.311 (8)	C(6)—C(5)—C(7)	122.9 (8)
O(10)—C(11)	1.46 (1)	C(2)—Fe—C(3)	42.5 (2)
C(5)—C(6)	1.52 (1)	C(3)—Fe—C(4)	39.6 (2)
C(5)—C(7)	1.49 (1)	C(4)—Fe—C(5)	38.1 (2)
C(16)—O(17)	1.12 (1)	Fe—C(16)—O(17)	176.1 (6)
C(18)—O(19)	1.12 (1)	Fe—C(11)—O(19)	178.5 (6)
C(20)—O(21)	1.13 (1)	Fe—C(20)—O(21)	176.3 (6)

Table 3. Mean planes of interest and deviations (\AA) of atoms from them

Least-squares mean planes were computed according to Blow (1960).

$$PL1: 0.6509x + 0.5661y - 0.5058z - 4.2518 = 0$$

C(2)*	-0.035 (7)	O(1)	0.475 (6)
C(3)*	0.057 (7)	C(8)	-0.362 (7)
C(4)*	-0.063 (7)	C(12)	0.095 (7)
C(5)*	0.045 (8)		($\chi^2 = 221$)

$$PL2: -0.3988x + 0.3405y - 0.8515z - 1.4377 = 0$$

C(4)*	-0.003 (7)	C(11)*	-0.001 (9)
C(8)*	0.013 (7)	C(3)	1.142 (6)
O(9)*	-0.003 (5)	C(5)	-1.142 (8)
O(10)*	-0.002 (5)		($\chi^2 = 4$)

$$PL3: 0.6648x + 0.3065y + 0.6814z - 1.9695 = 0$$

C(3)*	0.020 (7)	C(15)*	0.050 (10)
C(12)*	-0.019 (7)	C(2)	0.347 (7)
O(13)*	0.000 (5)	C(4)	-0.416 (7)
O(14)*	-0.014 (5)		($\chi^2 = 49$)

Dihedral angles ($^\circ$) (e.s.d.'s ca 0.8°)

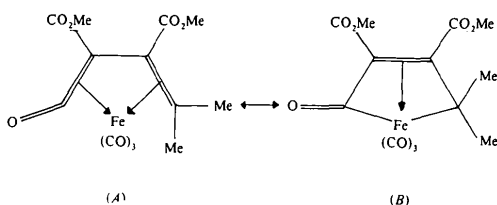
PL1/PL2	68.7	PL1/PL3	18.0	PL2/PL3	65.2
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* Atoms used to compute the mean plane.

Table 4. Selected geometric data (Å and deg) for complexes (1), (2), (3), (4) and (5)

The labelling schemes used in (2), (3), (4) and (5) are different from that of (1); all data have been converted according to (1).

Fe—C(2)	1.917 (2)	1.929 (6)	1.918 (3)	1.90 (1)	1.902 (7)
Fe—C(3)	2.135 (4)	2.109 (6)	2.107 (3)	2.182 (9)	2.082 (6)
Fe—C(4)	2.129 (4)	2.090 (5)	2.092 (3)	2.101 (9)	2.079 (5)
Fe—C(5)	2.168 (2)	2.235 (5)	2.201 (3)	2.105 (9)	2.213 (7)
O(1)—C(2)	1.191 (3)	1.188 (8)	—	1.21	1.187 (9)
C(2)—C(3)	1.469 (5)	1.442 (9)	1.439 (5)	1.48 (1)	1.454 (4)
C(3)—C(4)	1.415 (5)	1.407 (8)	1.397 (4)	1.41 (1)	1.411 (8)
C(4)—C(5)	1.433 (3)	1.416 (8)	1.414 (4)	1.43 (1)	1.408 (9)
Δ_2	0.036	0.022	0.029	0.045	0.020
O(1)—C(2)—C(3)	137.4 (4)	136.5 (6)	137	—	137.8 (7)



The canonical form (A) has a large contribution as indicated by the O(1)—C(2)—C(3) bond angle of 137.8 (7)°, intermediate between ideal values of 180° in (A) [C(2) sp hybridized] and 120° in (B) [C(2) sp^2 hybridized]. As shown in Table 4, the O(1)—C(2)—C(3) bond angle has about the same value in a number of other structures containing the vinylketene skeleton.

The Fe—C bond distances vary over a large range (1.902 to 2.213 Å), reflecting the fact that the metal—ligand back-bonding is stronger for the carbonyl C atom of the skeleton than for the other three C atoms of the η^4 system due to the electron-withdrawing O atom. The Fe—C(2) bond distances do not differ significantly in structures (1) to (5). As long as the substituent of C(3) is an H atom or an aliphatic C atom, the Fe—C(3) bond length does not change significantly; the bond length increases when the substituent is a C atom of a phenyl ring or an O atom of an OMe group. The same observation is true concerning the Fe—C(4) bond length where only the phenyl-substituted C atom differs significantly. In complexes (1), (3) and (4) atom C(5) has two methyl groups as substituents and consequently the corresponding Fe—C(5) bond distances are comparable. This bond length decreases when the substituent is an H atom or a phenyl group.

The bond-length variations of Fe—C(3), Fe—C(4) and Fe—C(5) in relation to the carbon substituent type can clearly be explained by the different electronic behaviour of the substituent atoms or groups.

In contrast to the variations of the Fe—C bond distances in going from (1) to (5) the skeleton C—C bond distances are not significantly different at the 3 σ level: the C(2)—C(3) bond remains between 1.439 and 1.48 Å, C(3)—C(4) between 1.397 and 1.415 Å and

C(4)—C(5) between 1.408 and 1.433 Å, leading to typical Δ_2 parameters (Cotton, Day, Frenz, Hardcastle & Troup, 1973) between 0.020 and 0.045 Å for 1–4- η dieneiron tricarbonyl complexes.

In contrast to the skeleton bond distances, the bond angles reflect the differences in Fe—C distances: angles C(2)—C(3)—C(4) and C(3)—C(4)—C(5) increase when the Fe—C(3) and Fe—C(4) bond lengths decrease.

As expected, and shown in Table 3 (plane PL1), the C atoms of the skeleton are reasonably planar; the dihedral angle C(2)—C(3)—C(4)—C(5) is 14.3°. C(8) and C(12) are out of the mean-plane PL1 by –0.362 (7) and 0.095 (7) Å respectively.

The two –CO₂Me groups are planar, as shown in Table 3 (planes PL2 and PL3). PL2 and PL3 are pseudo mirror planes for C atoms C(3)/C(5) and C(2)/C(4).

The Fe(CO)₃ group has normal geometry with Fe—C bond lengths in the range 1.768 to 1.827 Å and normal C—O distances.

The crystal structures of various complexes containing the vinylketene moiety with different substituents show that the overall geometry of the ligand is always the same, but a detailed analysis reveals important differences in bond lengths and angles related to the nature of the substituents.

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Complexe de Sodium de l'Ionophore Monensine B Monohydraté

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Abstract

A sodium complex of monensin B isolated and purified by chromatography has crystallized as a monohydrate (Mon B)Na.H₂O, C₃₅H₅₉NaO₁₁.H₂O, $M_r = 696.8$. The cell is orthorhombic, space group $P2_12_12_1$, with $a = 12.135$ (1), $b = 14.976$ (2), $c = 20.683$ (1) Å, $V = 3758.8$ Å³, $Z = 4$, $D_x = 1.23$ Mg m⁻³, $F(000) = 1580$. The structure has been refined to $R = 0.029$ (for 107 atoms) for 2349 observed reflexions. The heterocyclic part of the anion wraps the cation which is coordinated to six O atoms; two hydrogen bonds between the carboxylate group of one end and the two hydroxyl groups of the other end close the anionic ring. This conformation is very similar to that already known for complexes of monensin A. The water molecule is hydrogen bonded to two anions in a new mode compared to the cell organization of the other complexes.

Introduction

La monensine est un polyéther monocarboxylique doué de propriétés antibiotiques (utilisées contre la coccidiose du poulet) et ionophores (complexation et transport de cations monovalents à travers les membranes, avec spécificité marquée pour les ions Na⁺). En fait, le produit naturel extrait du *Streptomyces monensis* est un mélange des formes voisines A, B et C séparables par chromatographie.

Les structures cristallines actuellement déterminées sont toutes de monensine A, sous forme d'acide libre monohydraté (Lutz, Winkler & Dunitz, 1971) ou sous forme de complexe: (1) anhydre et dihydraté avec le sodium (Duax, Smith & Strong, 1980), (2) anhydre avec le bromure de sodium (Ward, Wei, Hoogerheide & Popov, 1978), (3) dihydraté avec l'argent (Pinkerton & Steinrauf, 1970); les trois dernières structures sont isomorphes. On connaît de plus les mailles de plusieurs autres complexes cristallisés.

Le complexe de sodium monohydraté décrit ci-après est le premier de monensine B, laquelle se différencie de la monensine A par le remplacement d'un groupement éthyle par un groupement méthyle.

Pour plus de commodité, les diverses molécules seront désignées dans ce qui suit par (Mon X)-M.xH₂O (X = A ou B, M = cation monovalent).

Partie expérimentale

La monensine provient d'un don gracieux des Laboratoires Eli Lilly (France). Les complexes de sodium, surtout des formes A et B, ont été séparés sur colonne de chromatographie {gel de silice [Silica Gel (Merck) 0,063–0,200 mm]}, avec un mélange éther-éthanol à 95% ($v:v = 0,97:0,03$) comme éluant. La chromatographie en couche mince a confirmé la pureté de la fraction (Mon B)Na (Haney & Hoehn, 1967) recristallisée ensuite dans le méthanol [p.f.(micro.) 526–531 K]. Des deux formes, seule (Mon B)Na a