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Tricarbonyl{(4—7-η)-3-acetyl-3a,7a-dihydro-6-methoxy-2-methylbenzo[*b*]furan)}-iron(0), $C_{15}H_{14}FeO_6$

BY BRYAN F. ANDERSON† AND GLEN B. ROBERTSON

Research School of Chemistry, The Australian National University, PO Box 4, *Canberra, ACT, Australia* 2600

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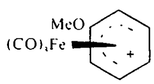
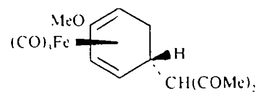
Abstract. $M_r = 346\cdot12$, monoclinic, $P2_1/c$, $a = 10\cdot258$ (1), $b = 8\cdot074$ (1), $c = 19\cdot290$ (2) Å, $\beta = 100\cdot97$ (1)° (293K), $U = 1568\cdot5$ Å^3, $Z = 4$, $D_x = 1\cdot466$ Mg m^{-3}, $F(000) = 712$, μ(Cu $K\alpha$) = $8\cdot160$ mm^{-1}. Refinement converged with $R = 0\cdot039$, $R_w = 0\cdot044$ for 1689 diffractometer data [$I \geq 3\sigma(I)$]. The metal–ligand bonding is typical of (1,3-diene)tricarbonyliron complexes. The dihydrofuran ring is *exo* to the metal ion.

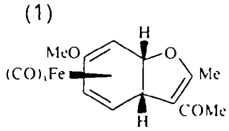
Introduction. The title compound (3) was prepared by A. J. Birch and co-workers by reaction of the tricarbonyl(cyclohexadienyl)iron cation (1) with acetyl-acetone, to give the β-diketone (2), followed by reaction of (2) with activated MnO_2 to give the product (3) (Birch, Chamberlain & Thompson, 1973).



(1)



(2)



(3)

Structures (2) and (3) were assigned from spectral and chemical data including deuteration experiments which indicated (*a*) *exo* attack of the nucleophile on (1) and (*b*) that the oxidative cyclization leading to (3) occurs with specific loss of the 6-*endo* proton. The present work serves to confirm the stereochemistry of both (2) and (3) and the *exo* attack of the nucleophile, suggested by Birch *et al.* as likely to be general for this class of reaction.

Experimental. Pale-yellow prismatic crystals (from chloroform), $0\cdot34 \times 0\cdot12 \times 0\cdot36$ mm parallel to **a***, **b** and **c*** respectively, bounding faces {100}, {001}, (010), ($0\bar{1}\bar{6}$) and ($0\bar{2}\bar{3}$); systematic absences ($h0l$ for l odd, $0k0$ for k odd) define $P2_1/c$ uniquely; Picker FACS-1 diffractometer, θ–2θ continuous-scan mode [scan velocity 2°min^{-1} 2θ, 2×10s background measurements at extremes, $3° < 2\theta < 127°$, Cu $K\alpha$ radiation, graphite-crystal monochromator, forms recorded $h, -k, \pm l$, 3133 reflections including standards (3 every 40 data)], data corrected for absorption (de Meulenaer & Tompa, 1965) but not for crystal degradation (*ca* 5%) or for extinction; sorting and averaging yielded 1689 unique data with $I \geq 3\sigma(I)$; R_s for this data set (Robertson & Whimp, 1975) was 0·024; cell dimensions and associated standard-error estimates derive from least-squares analysis of the setting angles for twelve well separated reflections in the range $69° < 2\theta < 91°$ [Cu $K\alpha_1$ radiation, $T = 293$K]; structure solved using *MULTAN* (Germain, Main & Woolfson, 1971), H atoms located from a difference synthesis, full-matrix least-squares refinement, $[\sigma(I)F_o/2I]^{-2}$ weights [$\rho^2 = 0\cdot002$ assumed (Busing & Levy, 1957; Corfield, Doedens & Ibers, 1967)], anisotropic thermal parameters for Fe, C and O, isotropic thermal parameters for H, $R = 0\cdot039$, $R_w = 0\cdot044$, $[\sum w\Delta^2/(n-s)]^{1/2} = 1\cdot45$; a final difference synthesis revealed no electron density excursions exceeding $\pm 0\cdot31$ eÅ^{-3}; scattering factors, and dispersion corrections for Fe, C and O, from *International Tables for X-ray Crystallography* (1974); calculations performed using *ANUCRYS* programs (McLaughlin, Taylor & Whimp, 1977) and the Australian National University Univac 1100/82 computer.

Discussion. Atom nomenclature is defined in Fig. 1 (*ORTEP* II, Johnson, 1976) and the corresponding coordinates are listed in Table 1.* Bond distances and angles are in Table 2.

Details of the metal–ligand bonding arrangement in (3) agree well with those reported for other tricarbonyl(1,3-cyclohexadiene)iron derivatives (Dunand & Robertson, 1982, and references therein). The (diene)Fe(CO)$_3$ moiety has approximate C_s symmetry. As is generally observed, the best planes through

† Present address: Department of Chemistry, Biochemistry and Biophysics, Massey University, Palmerston North, New Zealand.

* Lists of structure factors, anisotropic thermal parameters and atom deviations from the diene and dihydrofuran ring planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38079 (9 pp). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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the carbonyl [C(14),C(16),C(18)] and diene [C(4),C(5),C(6),C(7)] sets are not parallel, but are inclined [dihedral angle, 15·4 (3)°] so as to bring the unique carbonyl ligand closer to the diene plane. Moreover, the intercarbonyl angles to the unique ligand [av. 101·1 (2)°] substantially exceed that between

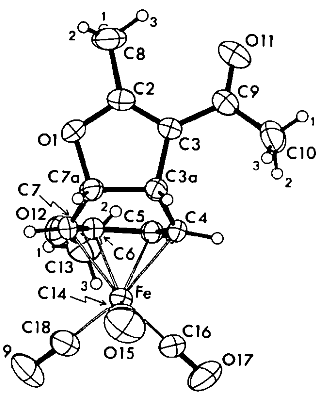

Fig. 1. Atom nomenclature in (3). H atoms are numbered for attached C atoms. Vibration ellipsoids correspond to 30% probability surfaces. H atoms are depicted as 0·11Å radius spheres.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

$B_{eq} = \frac{1}{3}\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$; actual B values for H atoms.

	x	y	z	B_{eq}(Å^2)
Fe	0·1376 (1)	0·2311 (1)	0·3874 (1)	4·6
O(1)	0·5305 (2)	0·0560 (3)	0·4103 (1)	5·4
C(2)	0·5724 (4)	0·1036 (5)	0·3504 (2)	4·8
C(3)	0·4751 (3)	0·1237 (5)	0·2937 (2)	4·0
C(3a)	0·3429 (4)	0·0913 (5)	0·3147 (2)	4·0
C(4)	0·2504 (3)	0·2365 (5)	0·3083 (2)	3·9
C(5)	0·2806 (3)	0·3742 (5)	0·3548 (2)	4·1
C(6)	0·3254 (3)	0·3298 (5)	0·4255 (2)	4·2
C(7)	0·3263 (4)	0·1573 (5)	0·4395 (2)	4·4
C(7a)	0·3835 (4)	0·0449 (5)	0·3930 (2)	4·4
C(8)	0·7201 (5)	0·1169 (11)	0·3607 (4)	7·3
C(9)	0·4976 (4)	0·1591 (5)	0·2233 (2)	4·8
C(10)	0·3848 (7)	0·1322 (12)	0·1634 (3)	7·7
O(11)	0·6048 (3)	0·2035 (4)	0·2109 (2)	6·6
O(12)	0·3577 (3)	0·4352 (4)	0·4813 (1)	6·1
C(13)	0·3236 (7)	0·6079 (8)	0·4681 (4)	7·7
C(14)	0·0755 (5)	0·0285 (8)	0·3648 (3)	6·8
O(15)	0·0394 (4)	−0·1037 (5)	0·3499 (2)	10·2
C(16)	0·0074 (4)	0·3553 (7)	0·3398 (2)	6·4
O(17)	−0·0736 (3)	0·4408 (6)	0·3106 (2)	10·2
C(18)	0·0813 (5)	0·2638 (7)	0·4678 (3)	7·7
O(19)	0·0488 (5)	0·2853 (6)	0·5208 (2)	12·4
H(3a)	0·302 (3)	−0·001 (4)	0·292 (2)	3·6 (8)
H(4)	0·208 (4)	0·262 (4)	0·260 (2)	5·9 (9)
H(5)	0·266 (3)	0·481 (4)	0·342 (1)	1·9 (6)
H(7)	0·341 (3)	0·124 (4)	0·485 (2)	5·2 (9)
H(7a)	0·361 (3)	−0·068 (4)	0·399 (2)	3·7 (8)
H(81)	0·737 (9)	0·214 (9)	0·376 (4)	15·2 (33)
H(82)	0·775 (7)	0·032 (9)	0·383 (3)	13·4 (27)
H(83)	0·750 (5)	0·117 (6)	0·315 (2)	9·9 (16)
H(101)	0·409 (5)	0·125 (7)	0·123 (3)	9·7 (15)
H(102)	0·304 (7)	0·186 (8)	0·168 (3)	10·9 (20)
H(103)	0·332 (7)	0·054 (7)	0·165 (3)	10·2 (23)
H(131)	0·353 (6)	0·660 (7)	0·519 (3)	11·0 (16)
H(132)	0·383 (6)	0·645 (7)	0·428 (3)	11·3 (18)
H(133)	0·230 (4)	0·614 (6)	0·458 (2)	7·1 (13)

Table 2. *Bond lengths* (Å) *and angles* (°)

Fe–C(4)	2·084 (4)	C(6)–C(7)	1·419 (6)
Fe–C(5)	2·058 (4)	C(6)–O(12)	1·363 (5)
Fe–C(6)	2·085 (4)	C(7)–C(7a)	1·474 (6)
Fe–C(7)	2·091 (4)	C(7)–H(7)	0·90 (3)
Fe–C(14)	1·779 (6)	C(7a)–H(7a)	0·95 (3)
Fe–C(16)	1·779 (5)	C(8)–H(81)	0·85 (8)
Fe–C(18)	1·774 (6)	C(8)–H(82)	0·86 (7)
O(1)–C(2)	1·363 (5)	C(8)–H(83)	0·98 (5)
O(1)–C(7a)	1·484 (4)	C(9)–C(10)	1·488 (7)
C(2)–C(3)	1·342 (5)	C(9)–O(11)	1·222 (6)
C(2)–C(8)	1·494 (6)	C(10)–H(101)	0·87 (5)
C(3)–C(3a)	1·509 (5)	C(10)–H(102)	0·96 (7)
C(3)–C(9)	1·450 (6)	C(10)–H(103)	0·83 (7)
C(3a)–C(7a)	1·536 (5)	O(12)–C(13)	1·449 (7)
C(3a)–C(4)	1·499 (5)	C(13)–H(131)	1·05 (5)
C(3a)–H(3a)	0·92 (3)	C(13)–H(132)	1·12 (6)
C(4)–C(5)	1·425 (5)	C(13)–H(133)	0·95 (5)
C(4)–H(4)	0·96 (4)	C(14)–O(15)	1·149 (7)
C(5)–C(6)	1·400 (5)	C(16)–O(17)	1·143 (6)
C(5)–H(5)	0·91 (3)	C(18)–O(19)	1·147 (7)
C(4)–Fe–C(5)	40·2 (1)	C(4)–C(5)–H(5)	124 (2)
C(5)–Fe–C(6)	39·5 (1)	C(6)–C(5)–H(5)	122 (2)
C(6)–Fe–C(7)	39·7 (2)	C(5)–C(6)–C(7)	115·2 (3)
C(14)–Fe–C(16)	101·1 (2)	C(5)–C(6)–O(12)	126·5 (4)
C(14)–Fe–C(18)	101·0 (2)	C(7)–C(6)–O(12)	118·0 (3)
C(16)–Fe–C(18)	91·7 (2)	C(6)–C(7)–C(7a)	118·5 (4)
C(2)–O(1)–C(7a)	107·3 (3)	C(6)–C(7)–H(7)	118 (2)
O(1)–C(2)–C(3)	114·7 (3)	C(7a)–C(7)–H(7)	113 (2)
O(1)–C(2)–C(8)	112·5 (4)	C(7)–C(7a)–O(1)	109·3 (3)
C(3)–C(2)–C(8)	132·7 (5)	C(7)–C(7a)–C(3a)	112·6 (3)
C(2)–C(3)–C(3a)	109·2 (3)	C(7)–C(7a)–H(7a)	112 (2)
C(2)–C(3)–C(9)	124·1 (4)	C(3a)–C(7a)–O(1)	106·2 (3)
C(3a)–C(3)–C(9)	126·6 (3)	C(3a)–C(7a)–H(7a)	109 (2)
C(3)–C(3a)–C(4)	115·4 (3)	O(1)–C(7a)–H(7a)	107 (2)
C(3)–C(3a)–C(7a)	102·5 (3)	C(3)–C(9)–C(10)	117·4 (4)
C(3)–C(3a)–H(3a)	111 (2)	C(3)–C(9)–O(11)	123·4 (3)
C(4)–C(3a)–C(7a)	108·7 (3)	C(10)–C(9)–O(11)	119·2 (4)
C(4)–C(3a)–H(3a)	112 (2)	C(6)–O(12)–C(13)	116·6 (4)
C(7a)–C(3a)–H(3a)	107 (2)	Fe–C(14)–O(15)	177·8 (5)
C(3a)–C(4)–C(5)	120·0 (3)	Fe–C(16)–O(17)	177·2 (5)
C(3a)–C(4)–H(4)	114 (2)	Fe–C(18)–O(19)	177·9 (4)
C(5)–C(4)–H(4)	116 (2)	C,O–C(Me)–H	109 (5)
C(4)–C(5)–C(6)	113·9 (4)	H–C(Me)–H	109 (13)

C(16) and C(18) [C(16)–Fe–C(18), 91·7 (2)°]. The origin of both effects appears to be steric since, together, they serve to generate nearly equal C(diene)–C(carbonyl) non-bonding interactions to each of the carbonyl ligands [C···C, 2·77–2·89 Å].

The diene set C(4),C(5),C(6),C(7) is just slightly aplanar [torsion angle, 3·3 (5)°] with the H and methoxy substituents each displaced significantly towards the Fe atom.* The set C(7),C(7a),C(3a), C(4) is also just marginally aplanar [torsion angle, 2·4 (4)°]. The interplane dihedral angle [C(4),C(5),C(6),C(7) ∧ C(7),C(7a),C(3a),C(4) = 41·7 (3)°] lies towards the high end of the reported range (Dunand & Robertson, 1982), such high-range values being characteristic for systems containing electron-donating and/or electron-withdrawing ring substituents.

The dihydrofuran ring is planar to within experimental error. The dihedral angle to the C(7),C(7a),C(3a),C(4) set is 59·0 (3)° and to the (diene) C(4),C(5),C(6),C(7) set is 100·7 (3)°, corresponding to an overall fold exceeding 90°. C(8), of the methyl substituent, is coplanar with the heterocycle

* See previous footnote.

but all atoms of the acetyl group are significantly out of plane [Δ(max.), 0·503(10) Å]. Nevertheless, C(9) is just 0·122 (4) Å and O(11) just 0·032 (3) Å out of plane, thereby maintaining a planar conjugation pathway O(1)—C(2)=C(3)—C(9)=O(11). A similar furan–carbonyl pathway, but with the formal double bonds *trans* rather than *cis*, has been reported in dimethyl 3a,4,9,9a-tetrahydro-9-oxo-*cis*-furo[3,2-*b*]quinoline-2,3-dicarboxylate (4) (Ueda, Ishiguro, Funakoshi, Saeki & Hamana, 1980). Bond distances, both for the five-atom conjugated systems and for the dihydrofuran moieties generally, agree closely in both molecules. Particularly noteworthy are the shortness of the O(1)—C(2) bond (present nomenclature, Ueda *et al.* values given second) [1·363 (5) and 1·353 (3) Å] and the angular deformations at C(3a) and C(2) [C(7a)—C(3a)—C(3), 102·5 (3) and 100·5 (2)°; O(1)—C(2)—C(3), 114·7 (3) and 115·0 (2)°; C(8)—C(2)—C(3), 132·7 (5) and 131·3 (2)°].

The four-atom C(3)-acetyl set exhibits a small pyramidal distortion with the central carbon [C(9)] displaced 0·018 (4) Å from the C(3),C(10),O(11) plane. Such distortions are often associated with short O···C=O or N···C=O contacts (Bürgi, Dunitz & Shefter, 1973, 1974; Dunand & Robertson, 1982) and thought to typify points along the reaction pathway for nucleophilic attack (Bürgi *et al.*, 1973, 1974). No such interactions are apparent in the present compound, and in this instance the deformation appears to be due to a series of weak intermolecular non-bonding interactions [O···H and O···C] to O(11).

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Dicytosinium Tetrachlorozincate, $[C_4H_6N_3O]_2[ZnCl_4]$

By P. E. Bourne* and Max R. Taylor†

School of Physical Sciences, The Flinders University of South Australia, Bedford Park, SA, 5042 *Australia*

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Abstract. $M_r = 431·42$, triclinic, $P\bar{1}$, $a = 17·86$ (1), $b = 6·86$ (1), $c = 6·87$ (1) Å, $\alpha = 80·20$ (7), $\beta = 103·90$ (9), $\gamma = 101·63$ (6)°, $U = 794·1$ Å^3, $Z = 2$, $D_m = 1·79$ (2), $D_x = 1·80$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2·13$ mm^{-1}, $F(000) = 432$, $T = 298$ K. Final $R = 0·079$ for 4495 unique reflections. Each type of crystallographically unique cation is in a separate band in the structure. In one of these bands there is strong interaction between carbonyl groups of centrosymmetrically related cations. The bands are interleaved by tetrahedral tetrachlorozincate anions.

Introduction. This compound was isolated and its structure was determined in the course of a study of pyrimidine–metal-ion interactions.

Experimental. Excess, freshly precipitated zinc hydroxide, suspended in methanol, was added to cytosine dissolved in a 50:50 water:ethanol mixture and sufficient hydrochloric acid to clear the solution was added. After several days of slow evaporation colourless crystals with two different morphologies appeared; one type was identified as cytosine monohydrate and the other is the subject of this analysis. The crystals decomposed in air and were sealed in glass capillary tubes for all X-ray diffraction experiments.

The $\bar{1}$ diffraction symmetry obtained from precession photographs indicated that the crystal system was

* Present address: College of Physicians and Surgeons, Department of Biochemistry, Columbia University, NY, 10032, USA.

† To whom correspondence should be addressed.

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