$[Cu(C_{16}H_{27}N_3O_2)]$

Characterization of the coordinated ligand moiety as 'en····ate' is supported by comparison of the C(2)—C(3), C(12)—C(13) distances with those of C(3)—C(4), C(13)—C(14). However both C—O distances are decidedly carbonyl. C(4)—N(2) and C(14)—N(3) appear to be imine bonds relative to the amine bonds of C(6)—N(2) and C(8)—N(4) or C(16)—N(3) and C(18)—N(4). The nearly perfect twofold axis down the N(4)—Cu vector is noteworthy.

References

ADDISON, A. W., RAO, T. N., REEDIJK, J., VAN RIJN, J. & VERSCHOOR, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

CUMMINGS, S. C., BRAYDICH, M. D. & FORTMAN, J. J. (1983). *Inorg. Chem.* **22**, 484–490.

CUMMINGS, S. C., CHEN, Y. Y., CHU, D. E., McKINNEY, B. D. & WILLIS, L. F. (1981). *Inorg. Chem.* **20**, 1885–1892, 3582.

CUMMINGS, S. C. & WALLIS, W. N. (1974). *Inorg. Chem.* **13**, 988–991.

FRENZ, B. A. (1983). *Enraf–Nonius Structure Determination Package.* College Station, Texas, USA, and Enraf–Nonius, Delft, The Netherlands.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

WALKER, N. & STUART, D. (1983). *Acta Cryst.* A**39**, 159–166.

Acta Cryst. (1987). C**43**, 2058–2060

Structure of Tricarbonyl(η^4-*syn*-1,4-diacetoxy-1,3-butadiene)iron(0)*

BY M. SORIANO-GARCÍA,† C. ALVAREZ AND R. A. TOSCANO

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán 04510, Mexico DF

AND A. C. CANO

Facultad de Estudios Superiores, Cuautitlán, Sección de Química Orgánica, Campo 1, Cuautitlán Izcalli, Mexico

Abstract. [Fe(CO)$_3$(C$_8$H$_{10}$O$_4$)], $M_r = 310.0$, monoclinic, $P2_1/n$, $a = 11.093$ (4), $b = 10.680$ (3), $c = 11.763$ (5) Å, $\beta = 101.45$ (3)°, $V = 1366$ (1) Å^3, $Z = 4$, $D_x = 1.51$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 1.124$ mm^{-1}, $F(000) = 632$, $T = 293$ K, $R = 0.046$ for 1888 observed reflections. The molecular structure is determined from the X-ray data and confirms the structure previously assigned on the basis of IR and NMR spectra. The Fe(CO)$_3$ group is symmetrically bonded to the butadiene moiety formed by C(4) to C(7) of the ligand. Both ester groups at C(4) and C(7) are planar and *cis* to each other about the central C(5)—C(6) bond. The structure consists of discrete molecules held in the crystal by van der Waals forces.

Introduction. As part of our investigations of complexes between Fe(CO)$_3$ and vinyl ester ligands, the title compound (1) was synthesized. Several complexes between Fe(CO)$_3$ and the vinyl ligand with various substituents including phenyl, ester and acyl groups

have been prepared in order to study their molecular conformation and chemical reactivity. The structure determination was undertaken to elucidate the stereochemistry of (1).
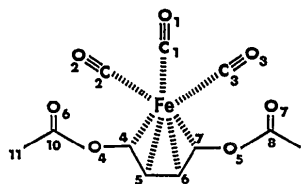
(1)

Experimental. The title compound (1) was obtained from the reaction of *trans,trans*-1,4-diacetoxy-butadiene (1.7 g, 10 mmol) (prepared as described by Hill & Carlson, 1964) and Fe(CO)$_5$ (9.7 g, 50 mmol) which was irradiated with an ultraviolet lamp of 200 W at room temperature. The product is purified by chromatographic methods and recrystallized from ethyl acetate to give yellow air-stable crystals with a composition of Fe(C$_{11}$H$_{10}$O$_7$).

Yellow crystal $0.30 \times 0.30 \times 0.40$ mm. Nicolet $R3$ four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters from 25 machine-centred reflections with $4.6 < 2\theta < 19.5°$, 2408 reflections with $3 < 2\theta < 50°$ for two octants, 1888 independent with $I > 2.5\sigma(I)$, index range $h \pm 13$, $k\,0$ ·12, $l\,0$ ·13, ω-scan mode, variable scan speed, scan width $1.0°$ (θ), two standard reflections monitored every 50 measurements, Lp correction and absorption ignored. Structure solved by heavy-atom method. Least-squares refinement of all non-H atoms treated anisotropically; H atoms riding on bonded C with fixed isotropic temperature factor, $U = 0.06$ Å^2. $\sum w|\Delta F|^2$ minimized with $w = [\sigma^2(F_o) + 0.001 \, (F_o)^2]^{-1}$, where σ is standard deviation of observed amplitudes, based on counting statistics; isotropic extinction parameter $X = 0.0016$. In the last cycle $(\Delta/\sigma)_{max} = 0.031$; $\Delta\rho$ from -0.40 to $+0.37$ e Å^{-3}; final $R = 0.046$, $wR = 0.058$; $S = 1.26$. Scattering factors from *International Tables for X-ray Crystallography* (1974). All computations performed on a Nova 4S computer and plots drawn on a Tektronix plotter with *SHELXTL* (Sheldrick, 1981).

Discussion. Atomic coordinates are given in Table 1.* Fig. 1 shows the conformation of (1). Bond lengths and selected angles for non-H atoms are listed in Table 2.

The diester vinyl ligand is complexed to the tricarbonyl iron unit as a four-electron ligand. The molecular arrangement thus bears a close similarity to those of butadieneiron tricarbonyl (Mills & Robinson, 1963), and tricarbonyl(dimethyl 4-methyl-1-oxo-1,3-pentadiene-2,3-dicarboxylate)iron (Fischer & Ricard, 1982), in which the iron atom adopts a square-pyramidal configuration.

The orientation of the Fe(CO)$_3$ group with respect to the butadiene moiety is such that one CO group [C(1)—O(1)] lies over the C(5)—C(6) bond, while the other two CO groups [C(2)—O(2) and C(3)—O(3)] lie over the C(4)—C(5) and C(6)—C(7) bonds. There is essentially mirror symmetry, with the mirror plane passing through the metal atom, one CO group [C(1)—O(1)] and the midpoint of the butadiene residue, as in butadieneiron tricarbonyl (Mills & Robinson, 1963). The arrangement of ligands about the metal atom can be described, approximately, as square pyramidal with the unique CO group [C(1)—O(1)], in this case, forming the quasifourfold axis, the base of the pyramid being formed by C(2) and C(3) of the carbonyl goups and C(4) and C(7) of the butadiene

system. The dihedral angle between planes formed by the O(1)—C(1)—Fe and C(4)—C(5)—C(6)—C(7) atoms is 75.4 (6)°.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å^2 $\times 10^3$)

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	U_{eq}
Fe	122 (1)	6868 (1)	6480 (1)	42 (1)
O(1)	−992 (3)	7396 (4)	4053 (3)	80 (1)
O(2)	2450 (3)	5717 (4)	6201 (4)	98 (2)
O(3)	−1015 (4)	4466 (3)	6854 (4)	100 (2)
O(4)	2115 (2)	8848 (3)	6465 (2)	50 (1)
O(5)	−2311 (2)	7185 (3)	7289 (2)	48 (1)
O(6)	1367 (3)	9502 (3)	4662 (2)	66 (1)
O(7)	−3396 (3)	7686 (4)	5534 (3)	73 (1)
C(1)	−551 (4)	7176 (4)	4983 (4)	53 (2)
C(2)	1548 (4)	6151 (4)	6328 (4)	62 (2)
C(3)	−557 (4)	5388 (4)	6714 (4)	65 (2)
C(4)	921 (3)	8670 (4)	6668 (3)	42 (1)
C(5)	896 (4)	8122 (4)	7751 (3)	50 (1)
C(6)	−229 (4)	7713 (4)	7954 (3)	47 (1)
C(7)	−1281 (3)	7849 (4)	7060 (3)	42 (1)
C(8)	−3341 (4)	7162 (4)	6437 (4)	47 (1)
C(9)	−4318 (4)	6400 (5)	6779 (5)	72 (2)
C(10)	2229 (4)	9279 (4)	5418 (3)	45 (1)
C(11)	3545 (4)	9416 (5)	5343 (4)	66 (2)

Table 2. *Bond lengths* (Å) *and selected angles* (°), *with e.s.d.'s in parentheses*

|			
Fe—C(1)	1.801 (4)	Fe—C(2)	1.798 (5)
Fe—C(3)	1.795 (5)	Fe—C(4)	2.112 (4)
Fe—C(5)	2.063 (4)	Fe—C(6)	2.059 (4)
Fe—C(7)	2.099 (4)	O(1)—C(1)	1.131 (5)
O(2)—C(2)	1.139 (6)	O(3)—C(3)	1.135 (6)
O(4)—C(4)	1.405 (5)	O(4)—C(10)	1.343 (5)
O(5)—C(7)	1.415 (5)	O(5)—C(8)	1.363 (4)
O(6)—C(10)	1.193 (4)	O(7)—C(8)	1.191 (5)
C(4)—C(5)	1.408 (5)	C(5)—C(6)	1.386 (6)
C(6)—C(7)	1.415 (5)	C(8)—C(9)	1.473 (7)
C(10)—C(11)	1.487 (6)		
C(1)—Fe—C(2)	100.6 (2)	C(1)—Fe—C(3)	101.9 (2)
C(2)—Fe—C(3)	92.6 (2)	C(1)—Fe—C(4)	91.1 (2)
C(2)—Fe—C(4)	92.2 (2)	C(3)—Fe—C(4)	165.1 (2)
C(2)—Fe—C(7)	165.6 (2)	C(1)—Fe—C(7)	92.0 (2)
C(4)—Fe—C(7)	80.4 (1)	C(3)—Fe—C(7)	91.6 (2)
C(5)—C(6)—C(7)	118.5 (3)	C(4)—C(5)—C(6)	117.8 (3)
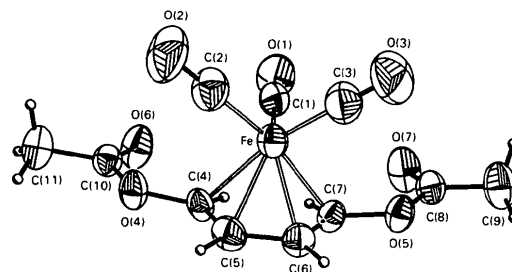
Fig. 1. The molecular conformation of the title compound, showing atom numbering. The thermal ellipsoids are drawn at the 50% probability level.

The diester vinyl unit can be represented by the resonance hybrid between the diene (A) and the $2\sigma-\pi$ complex (B).

CH₃OCO OCOCH₃
Fe
(CO)₃

(A)

⇌

CH₃OCO OCOCH₃
Fe
(CO)₃

(B)
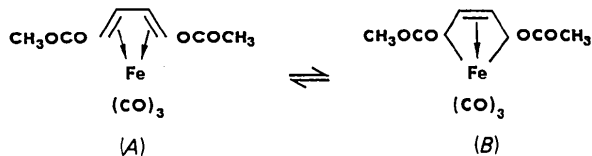
The canonical form (B) makes a large contribution as indicated by the C(5)—C(6) bond length which is shorter by 0·022 and 0·029 Å than those of C(4)—C(5) and C(6)—C(7).

The Fe—C bond distances vary over a small range [2·059 (4) to 2·112 (4) Å] reflecting the fact that the metal–ligand bonding is nearly the same for the four C atoms of the η^4 system.

The two CH₃COO— ester groups are cis to each other about the C(5)—C(6) bond. Both ester groups [C(11)—C(10)—O(6),O(4) and C(9)—C(8)—O(5),O(7)] are planar [to within ±0·004 (6) and ±0·015 (6) Å, respectively]. The dihedral angle between the two ester groups is 21·4 (6)°. The C(8)—O(7) and C(10)—O(6) bonds are shorter by 0·024 and 0·022 Å than the accepted value of 1·215 (5) Å for the C=O bond (Sutton, 1965); they are oriented cis to the C(4)—H and C(7)—H bonds, respectively (Mathieson, 1965; Chothia & Pauling, 1970).

The butadiene residue is planar within ±0·005 Å. The dihedral angles between the butadiene residue and the ester groups at C(4) and C(7) are 10·1 (5) and 11·3 (6)°, respectively.

The discrete molecules, as shown in Fig. 2, are held in the crystal by van der Waals forces.
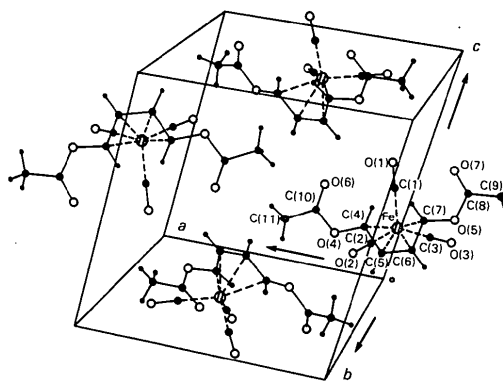

Fig. 2. A perspective drawing of the contents of one unit cell.

References

CHOTHIA, C. & PAULING, P. J. (1970). Nature (London), 226, 541–542.
FISCHER, J. & RICARD, L. (1982). Acta Cryst. B38, 1140–1144.
HILL, R. K. & CARLSON, R. M. (1964). J. Org. Chem. 30, 2414–2417.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
MATHIESON, A. McL. (1965). Tetrahedron Lett. pp. 4137–4144.
MILLS, O. S. & ROBINSON, G. (1963). Acta Cryst. 16, 758–761.
SHELDRICK, G. M. (1981). SHELXTL. Revision 3. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data. Univ. of Göttingen, Federal Republic of Germany.
SUTTON, L. E. (1965). Tables of Interatomic Distances and Configuration in Molecules and Ions. Spec. Publ. No. 18. London: The Chemical Society.

Structure of a Copper(II) Complex with a Chiral Schiff Base and a Chiral Aminoalcohol

BY KAZUNORI YANAGI AND MASAO MINOBE*

Takatsuki Research Laboratory, Sumitomo Chemical Co. Ltd, 2-10-1, Tsukahara, Takatsuki, Osaka 569, Japan

Abstract. [(R)-2-Amino-1,1-bis(2-methoxyphenyl)-3-phenyl-1-propanolato][(R)-1,1-bis(2-methoxyphenyl)-3-phenyl-2-salicylideneamino-1-propanolato]copper(II), [Cu(C₃₀H₂₇NO₄)(C₂₃H₂₅NO₃)], $M_r = 892\cdot6$, monoclinic, $P2_1$, $a = 11\cdot527$ (1), $b = 21\cdot081$ (1), c = 9·564 (1) Å, $\beta = 99\cdot01$ (1)°, $V = 2295\cdot3$ (6) Å³, $Z = 2$, $D_x = 1\cdot29$ Mg m⁻³, λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 1·073 mm⁻¹, $T = 295$ K, $F(000) = 938$, $R = 0\cdot029$ for 3852 observed reflections. The coordination geometry of the Cu atom is a distorted square pyramid (4 + 1). The tridentate Schiff-base group occupies three of the basal square-planar coordination sites and an N atom of the aminoalcohol

* Present address: Ehime Research Laboratory, Sumitomo Chemical Co. Ltd, 5–1, Sobiraki-cho, Niihama, Ehime 792, Japan.