

## Structure of $\mu$ -Carbonyl-dicarbonylbis( $\eta$ -cyclopentadienyl)- $\mu$ -(methylocyclopropylidene)-diiron(Fe–Fe)

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**Abstract.**  $[\text{Fe}_2(\text{C}_5\text{H}_5)_2(\text{CO})_3(\text{C}_4\text{H}_6)]$ ,  $M_r = 380.01$ , monoclinic,  $P2_1/n$ ,  $a = 8.884$  (3),  $b = 11.601$  (3),  $c = 15.021$  (4) Å,  $\beta = 102.85$  (2)°,  $V = 1509.3$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.672$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 19.3$  cm<sup>-1</sup>,  $F(000) = 776$ , room temperature [293 (2) K],  $R = 0.071$  for 685 independent observed reflections. The compound has an Fe–Fe backbone with a distance of 2.504 (2) Å, bridged by a  $\mu$ -carbonyl and one C atom from the methyl-substituted cyclopropylidene ring. Each Fe is also bonded to a linear carbonyl and a cyclopentadienyl ring which are in *cis* configuration with respect to the plane of the bridging ligands.

**Introduction.** The title material was synthesized as a model compound during investigation of an alternative mechanism proposed for C–C-bond-formation steps during Fischer–Tropsch synthesis (Brady & Pettit, 1980, 1981; Osterloh, Cornell & Pettit, 1982; McCandlish, 1983).

**Experimental.**  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})[\mu\text{-CCH}(\text{CH}_3)\text{CH}_2]$  crystallized from hexane; density not measured; crystal dimensions approximately 0.5 × 0.3 × 0.2 mm, cell dimensions calculated from setting angles of 25 accurately centered reflections,  $\theta$  range 3.3–13.3°, on Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo  $K\alpha$ ;  $\omega$ – $2\theta$  scan mode used to collect 4058 intensities with  $0 < \theta < 25^\circ$ ,  $h$ –10→10,  $k$ –2→16,  $l$ –2→17; scan range 3.62° ( $\pm$  calculated  $2\theta$  for  $K\alpha$ ), background counting time half scan-time, evenly divided either side of peak; 2591 independent reflections measured, only 685 observed [ $I > 2.5\sigma(I)$ ] (due to poor crystal quality and rapid intensity drop-off at high  $\theta$  values) (Frenz, 1982), absorption corrections using  $\psi$ -scan data, correction factor 0.94 to 0.99; three check reflections, monitored throughout data collection, showed 2.9% intensity gain overall; data set to one scale by

application of scaling factors computed from changes in intensities of standard reflections. Fe-atom positions obtained by direct methods; difference Fourier maps, least-squares structure-factor calculations used to position remaining non-H atoms. H atoms placed at calculated positions, isotropic temperature factors  $\beta = 4.0$  Å<sup>2</sup> not refined. Because of the low data/parameter ratio (3.06), during final cycles of least squares ten C atoms from the two cyclopentadienyl rings refined with isotropic thermal values. C(1) (the bridging C from the cyclopropylidene ring) also given isotropic thermal value because of unrealistic r.m.s. values when refined with anisotropic thermal factors; all remaining non-H atoms refined with anisotropic thermal factors. These parameter constraints resulted in refinement converging at the relatively high values  $R = 0.071$  and  $wR = 0.077$ ;  $w = 1/\sigma|F_o|^2$ , quality of fit 1.35;  $\Delta/\sigma < 0.1$ ; final cycle of least-squares refinement minimizing  $\sum w(\Delta F)^2$  contained 685 observations and gave a difference Fourier map showing no feature greater than 0.72 e Å<sup>-3</sup>. No correction for secondary extinction. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Final positional and equivalent isotropic thermal parameters are in Table 1, major bond lengths and angles in Table 2.\*

**Discussion.** The four  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})[\mu\text{-CCH}(\text{CH}_3)\text{CH}_2]$  (I) clusters are situated on the general positions in the space group  $P2_1/n$ . Each cluster has an Fe–Fe backbone straddled by a bridged carbonyl and one C atom from the cyclopropylidene ring (Fig. 1). The contents of a unit cell are shown in

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42567 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters and their *e.s.d.*'s

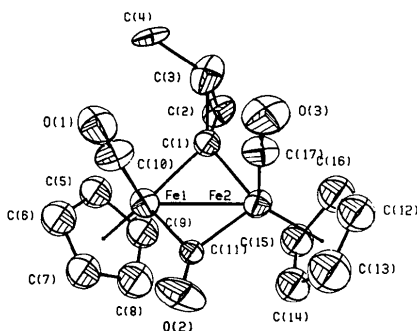
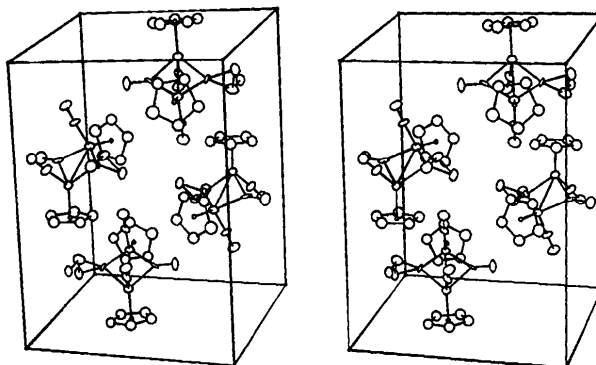
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )
Fe(1)	0.6630 (4)	0.2994 (3)	0.9529 (2)	3.07 (7)
Fe(2)	0.8500 (3)	0.2520 (3)	0.8557 (2)	3.00 (6)
C(1)	0.681 (2)	0.163 (2)	0.882 (1)	2.8 (4)*
C(2)	0.675 (3)	0.034 (2)	0.910 (2)	4.1 (6)
C(3)	0.565 (3)	0.082 (2)	0.825 (2)	4.7 (6)
C(4)	0.397 (2)	0.087 (2)	0.824 (1)	3.8 (6)
C(5)	0.589 (2)	0.223 (2)	1.065 (1)	4.4 (5)*
C(6)	0.548 (3)	0.340 (2)	1.057 (2)	5.0 (6)*
C(7)	0.678 (3)	0.403 (2)	1.068 (2)	4.8 (6)*
C(8)	0.806 (3)	0.332 (2)	1.084 (2)	5.5 (6)*
C(9)	0.754 (3)	0.221 (2)	1.081 (1)	4.6 (5)*
C(10)	0.505 (2)	0.345 (2)	0.865 (1)	3.8 (6)
C(11)	0.795 (2)	0.396 (2)	0.896 (1)	2.1 (4)*
C(12)	1.032 (3)	0.200 (2)	0.800 (2)	5.2 (6)*
C(13)	1.073 (3)	0.299 (2)	0.849 (2)	6.8 (7)*
C(14)	1.076 (2)	0.271 (2)	0.941 (1)	4.6 (5)*
C(15)	1.034 (3)	0.163 (2)	0.945 (2)	4.6 (6)*
C(16)	1.007 (3)	0.114 (2)	0.855 (2)	5.4 (6)*
C(17)	0.732 (2)	0.276 (2)	0.748 (1)	3.3 (5)
O(1)	0.414 (2)	0.377 (1)	0.8066 (9)	4.9 (4)
O(2)	0.823 (2)	0.494 (1)	0.895 (1)	6.3 (5)
O(3)	0.662 (2)	0.292 (1)	0.6747 (9)	5.4 (4)

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as:  $\frac{4}{3}a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}$ , where *a*, *b*, *c* are direct cell constants and *B*<sub>*ij*</sub> values are given in the supplemental tables.

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

Metal—metal	
Fe(1)—Fe(2)	2.504 (4)
Metal—C(carbonyl)	
Fe(1)—C(10)	1.781 (24)
Fe(2)—C(17)	1.744 (19)
Fe(1)—C(11)	1.949 (20)
Fe(2)—C(11)	1.885 (21)
Metal—C(methylcyclopropylidene ring)	
Fe(1)—C(1)	1.937 (18)
Fe(2)—C(1)	1.930 (19)
C—O(carbonyl)	
C(10)—O(1)	1.114 (21)
C(17)—O(3)	1.151 (8)
C(11)—O(2)	1.164 (18)
C—C(methylcyclopropylidene)	
C(1)—C(2)	1.557 (24)
C(1)—C(3)	1.507 (27)
C(2)—C(1)	1.523 (27)
C(3)—C(4)	1.486 (28)
C—C(cyclopentadiene)	
C(5)—C(6)	1.403 (26)
C(6)—C(7)	1.343 (27)
C(7)—C(8)	1.385 (28)
C(8)—C(9)	1.361 (26)
C(9)—C(5)	1.434 (26)
C(12)—C(13)	1.378 (28)
C(13)—C(14)	1.415 (28)
C(14)—C(15)	1.310 (26)
C(15)—C(16)	1.436 (28)
C(16)—C(12)	1.344 (29)
Around Metal	
C(1)—Fe(1)—C(11)	95.7 (8)
C(11)—Fe(1)—C(10)	87.5 (9)
C(1)—Fe(1)—C(10)	88.8 (9)
C(1)—Fe(2)—C(11)	98.0 (8)
C(1)—Fe(2)—C(17)	86.5 (8)
C(11)—Fe(2)—C(17)	90.9 (8)
Carbonyls (linear)	
Fe(1)—C(10)—O(1)	175.0 (10)
Fe(2)—C(17)—O(3)	176.2 (2.8)
Carbonyls (bridged)	
Fe(1)—C(11)—O(2)	136.0 (1.6)
Fe(2)—C(11)—O(2)	142.4 (1.6)
Around C	
Fe(1)—C(1)—Fe(2)	80.7 (7)
Fe(1)—C(11)—Fe(2)	81.5 (8)
Fe(1)—C(1)—C(3)	133.5 (2)
Fe(1)—C(1)—C(2)	128.3 (1.4)
Fe(2)—C(1)—C(3)	133.5 (1.5)
Fe(2)—C(1)—C(2)	130.0 (1.4)
C(2)—C(1)—C(3)	59.6 (1.2)
C(1)—C(2)—C(3)	58.6 (1.3)
C(1)—C(2)—C(3)	61.9 (1.3)
C(1)—C(3)—C(2)	122.9 (1.9)
C(2)—C(3)—C(4)	118.7 (2.1)
C(9)—C(5)—C(6)	105.2 (1.9)
C(5)—C(6)—C(7)	108.6 (2.0)
C(6)—C(7)—C(8)	110.2 (2.2)
C(7)—C(8)—C(9)	107.2 (2.2)
C(8)—C(9)—C(5)	108.6 (2.0)
C(16)—C(12)—C(13)	110.4 (2.3)
C(12)—C(13)—C(14)	105.7 (2.2)
C(13)—C(14)—C(15)	109.1 (2.1)
C(14)—C(15)—C(16)	108.8 (2.2)
C(15)—C(16)—C(12)	105.9 (2.2)

Fig. 2. Each Fe atom is also linked to a linear carbonyl atom and a cyclopentadienyl ring which are in *cis* configuration with respect to the plane containing the bridging ligands. Apart from the methyl substitutions of C(4) onto the cyclopropylidene ring, spatially this cluster bears many resemblances to the unsubstituted complex  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CCH}_2\text{CH}_2)$  (II) (Hoel, Ansell & Leta, 1984). There is a general lack of *m* symmetry in this cluster as indicated by the lack of equivalence of bonds and angles which are related by the *m* symmetry in (II). In this compound the deviation of C(4) from the mean plane through C(1), C(2), C(3), C(1) and O(2)  $[0.7985x - 0.2284y - 0.5570z - 5.1438 = 0$ ; the mirror plane in (II)] is 1.189 Å. The two Fe atoms are separated by a distance of 2.504 (4) Å, similar to that of 2.503 (7) Å in (II) but somewhat shorter than the 2.531 (2) and 2.534 (2) Å found in the *cis*- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$  (Bryan, Green, Newlands & Field, 1970) and its *trans* isomer *trans*- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$  (Bryan & Green, 1970). The Fe—C distances in the linear (av. 1.762 Å) and bridged (av. 1.917 Å) carbonyls are similar to

Fig. 1. ORTEP drawing (Johnson, 1976) of the molecular structure of *cis*- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CCH}(\text{CH}_3)\text{CH}_2)$ .Fig. 2. A stereoscopic view of *cis*- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CCH}(\text{CH}_3)\text{CH}_2)$ . The *b* axis is horizontal and the *c* axis vertical.

those in (II) (1.728 and 1.914 Å respectively). Within the cyclopropylidene ring the three C—C bonds range from 1.507 (27)–1.557 (24) Å (av. 1.529 Å) and probably reflect the three different steric environments of each ring C. The average C—C distance of 1.529 Å is somewhat larger than the three equal bond values in cyclopropane (1.509 Å) (Bastiansen, Fritsch & Hedberg, 1964). The C(3)—C(4)(methyl) distance of 1.486 (28) Å is similar to the ring C—methyl value of 1.51 Å in dimethyl 1,1'-dimethylbicyclopropyl-2,2'-dicarboxylate (Jongsma & Van der Meer, 1971).

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## Microporous Aluminophosphate Number 17 with Encapsulated Piperidine, Topological Similarity to Erionite

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**Abstract.** Aluminiumphosphate–piperidinehydrate,  $\text{Al}_{18}\text{P}_{18}\text{O}_{72}\cdot 4(\text{C}_5\text{H}_{11}\text{N}\cdot\text{H}_2\text{O})$ ,  $M_r = 2608$ , hexagonal,  $P6_3/m$ ,  $a = 13.2371$  (9),  $c = 14.7708$  (10) Å,  $V = 2241.4$  Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 1.93$  g cm<sup>-3</sup>,  $\lambda(\text{Cu K}\alpha) = 1.5418$  Å,  $\mu = 61$  cm<sup>-1</sup>,  $F(000) = 1312$ ,  $T \sim 295$  K,  $R = 0.086$  for 1146 diffractions. An aluminophosphate gel, produced from hydrated alumina and phosphoric acid, was digested with piperidine ( $\text{C}_5\text{H}_{10}\text{NH}$ ) for 1 week at 473 K to form  $\text{AlPO}_4\text{-17}$ . Al and P atoms alternate near the tetrahedral nodes of the erionite framework. An extraframework oxygen species in a partially occupied site bridges between a pair of Al atoms in the opposing 6-rings of each cancrinite cage. Each of the two ellipsoidal cavities contains two piperidine species. The nature of the charge on the extraframework oxygen species and the piperidine species is discussed.

**Introduction.** A new class of microporous materials was synthesized from aluminophosphate gels using a wide variety of organic amines and quaternary ammonium cations as templates (Wilson, Lok, Messina,

Cannan & Flanigen, 1982, 1983). Fourteen out of the twenty new materials are microporous after calcination to remove encapsulated organic material, and the tetrahedral frameworks with alternating Al and P include structural analogs of the aluminosilicate zeolites erionite ( $\text{AlPO}_4\text{-17}$ ) and sodalite ( $\text{AlPO}_4\text{-20}$ ). The novel framework of  $\text{AlPO}_4\text{-5}$  encloses non-connecting parallel channels bounded by 12-rings, and the as-synthesized material (Wilson, Lok & Flanigen, 1982) contains tetrapropylammonium hydroxide species in a tripod configuration (Bennett, Cohen, Flanigen, Pluth & Smith, 1983).

Four aluminophosphates prepared in the presence of an amine contain Al in 4-, 5- or 6-coordination with O. In two of them, the amine apparently fragmented during crystallization of the aluminophosphate framework. The potential template diaminebutane yielded  $\text{AlPO}_4\text{-15}$ ,  $\text{NH}_4\text{Al}_2(\text{OH})(\text{H}_2\text{O})(\text{PO}_4)_2\cdot 2\text{H}_2\text{O}$ , which has a tetramer of edge-sharing  $\text{AlO}_4(\text{OH})_2$  and vertex-sharing  $\text{AlO}_4(\text{OH})(\text{H}_2\text{O})$  octahedra sharing vertices with  $\text{PO}_4$  tetrahedra to form a framework 3-connected