Crystal and Molecular Structures of (η-Methylcyclopentadienyl)(η-7-*exo*-phenylcyclohepta-1,3,5-triene)manganese †

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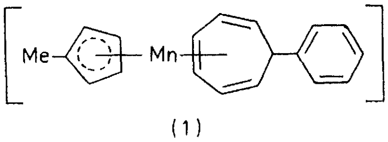
The crystal and molecular structure of the title compound have been determined by *X*-ray diffraction methods from photographic data assessed by a film scanner. Crystals are monoclinic, space group $P2_1/c$ with $Z = 4$, in a cell of dimensions $a = 7.54(1)$, $b = 11.77(2)$, $c = 16.42(2)$ Å, and $\beta = 80.6(2)°$. The structure has been solved by Patterson and Fourier methods, and refined by least-squares techniques to R 0.097 for 999 reflections.

COMPOUND (1) is prepared by irradiating with u.v. light a mixture of tricarbonyl(η-methylcyclopentadienyl)-manganese and 7-phenylcyclohepta-1,3,5-triene, the latter ligand displacing the three carbonyl groups and giving a mixture of the *endo* and *exo* isomers.[1] It is very soluble in the common organic solvents; it decomposes in air in a few minutes, but is stable *in vacuo*. This work was undertaken to confirm the stereochemistry assigned on spectroscopic grounds, and to define the geometry of the molecule.



(1)

EXPERIMENTAL

The sample was a tablet of dimensions *ca.* 0.5 × 0.3 × 0.4 mm.

Crystal Data.—$C_{19}H_{19}Mn$, $M = 302$, Monoclinic, $a = 7.54(1)$, $b = 11.77(2)$, $c = 16.42(2)$ Å, $\beta = 80.6(2)°$, $U = 1\,438$ Å^3, $D_m = 1.42 \pm 0.08$, $Z = 4$, $D_c = 1.40$, $F(000) = 632$, space group $P2_1/c$ (no. 14) from systematic absences, Cu-K_α radiation, $\lambda = 1.542$ Å, μ(Cu-K_α) = 73.6 cm^{-1}. The density was estimated by noting that a crystal floated in chloroform, but sank in dichloromethane; the substance was not stable enough to permit greater precision.

Crystallographic Measurements.—The symmetry and cell dimensions were obtained from rotation and Weissenberg photographs about *b* with Cu-K_α radiation. Intensity data for the layers *hkl* ($k = 0-10$) were collected as equi-inclination Weissenberg photographs with the crystal sealed in a capillary tube of Lindemann glass. Initially, these data were estimated visually, and 2 157 reflections, including unobserved ones assessed at one third the locally observable minimum,[2] were used to determine the structure. Subsequently intensities were measured at the S.R.C. Microdensitometer Laboratory; data for **999** reflections were provided. In each case the data were corrected for time of exposure and for Lorentz and polarization factors; in neither case was a correction made for absorption since the glass envelope prevented accurate measurement of the crystal size.

Structure Determination.—A three-dimensional Patterson map yielded co-ordinates for the manganese atom, and successive cycles of structure-factor calculations and Fourier syntheses revealed the remaining atoms. The structure-factor program automatically scales the data so that for each layer $\Sigma(\text{scaled}|F_o|) = \Sigma(|F_c|)$. Throughout

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† No reprints available.

[1] P. L. Pauson and J. A. Segal, *J.C.S. Dalton*, 1975, 2387.

[2] W. C. Hamilton, *Acta Cryst.*, 1955, **8**, 185.

these calculations and the later ones the scattering factors were corrected for the real component of anomalous dispersion. When the data from the film scanner were available, atom sites previously determined were entered, and

TABLE 1

Final co-ordinates ($\times$ 10^4) and their standard deviations

Atom	x/a	y/b	z/c
Mn(1)	114(3)	2 327(2)	868(1)
C(2)	−2 686(19)	2 027(12)	910(9)
C(3)	−1 654(23)	1 205(14)	398(10)
C(4)	−563(21)	1 782(13)	−263(9)
C(5)	−979(22)	2 943(14)	−162(10)
C(6)	−2 232(20)	3 117(12)	539(9)
C(7)	−3 052(27)	4 239(17)	843(12)
C(8)	250(22)	1 703(14)	2 085(10)
C(9)	1 329(25)	1 098(16)	1 489(12)
C(10)	2 604(27)	1 598(17)	836(12)
C(11)	2 849(26)	2 771(18)	609(12)
C(12)	1 810(28)	3 678(17)	1 009(13)
C(13)	570(23)	3 621(14)	1 737(10)
C(14)	807(21)	2 806(15)	2 440(10)
C(15)	2 574(19)	2 890(13)	2 760(9)
C(16)	3 440(24)	1 940(14)	2 990(11)
C(17)	4 996(26)	2 024(16)	3 346(11)
C(18)	5 665(25)	3 060(15)	3 489(11)
C(19)	4 733(26)	4 024(17)	3 291(12)
C(20)	3 213(24)	3 927(14)	2 909(11)

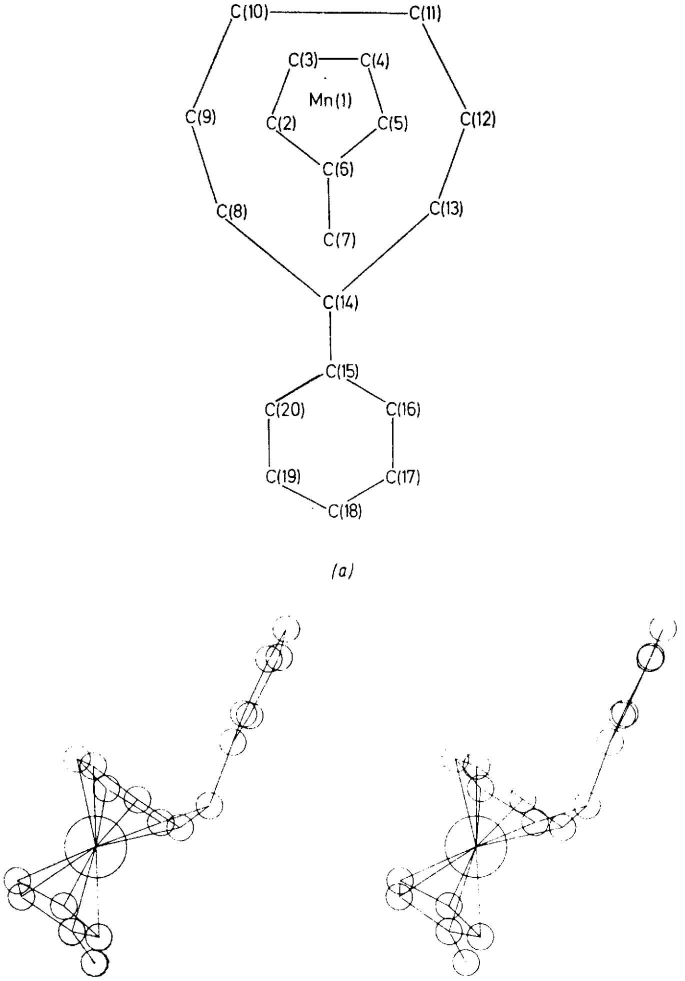

FIGURE 1 (*a*) The molecule showing the crystallographic numbering. (*b*) The molecule viewed down the *b* axis

TABLE 2

Bond lengths (Å) and angles (°)

(*a*) Lengths

Mn(1)–C(2)	2.13	C(2)–C(3)	1.43
Mn(1)–C(3)	2.11	C(2)–C(6)	1.44
Mn(1)–C(4)	2.10	C(3)–C(4)	1.42
Mn(1)–C(5)	2.13	C(4)–C(5)	1.41
Mn(1)–C(6)	2.14	C(5)–C(6)	1.38
		C(6)–C(7)	1.51
Mn(1)–C(8)	2.15	C(8)–C(9)	1.37
Mn(1)–C(9)	2.07	C(9)–C(10)	1.44
Mn(1)–C(10)	2.06	C(10)–C(11)	1.43
Mn(1)–C(11)	2.10	C(11)–C(12)	1.42
Mn(1)–C(12)	2.08	C(12)–C(13)	1.39
Mn(1)–C(13)	2.15	C(8)–C(14)	1.51
		C(13)–C(14	1.53
C(14)–C(15)	1.51		
C(15)–C(16)	1.38		
C(15)–C(20)	1.35		
C(16)–C(17)	1.40		
C(17)–C(18)	1.35		
C(18)–C(19)	1.40		
C(19)–C(20)	1.40		

(*b*) Angles

(*i*) At Mn

C(2)–Mn–C(3)	39	C(5)–Mn–C(6)	38
C(2)–Mn–C(4)	66	C(5)–Mn–C(8)	160
C(2)–Mn–C(5)	65	C(5)–Mn–C(9)	153
C(2)–Mn–C(6)	39	C(5)–Mn–C(10)	126
C(2)–Mn–C(8)	96	C(5)–Mn–C(11)	104
C(2)–Mn–C(9)	113	C(5)–Mn–C(12)	99
C(2)–Mn–C(10)	146	C(5)–Mn–C(13)	114
C(2)–Mn–C(11)	169		
C(2)–Mn–C(12)	138	C(6)–Mn–C(8)	123
C(2)–Mn–C(13)	111	C(6)–Mn–C(9)	151
		C(6)–Mn–C(10)	164
C(3)–Mn–C(4)	40	C(6)–Mn–C(11)	132
C(3)–Mn–C(5)	65	C(6)–Mn–C(12)	104
C(3)–Mn–C(6)	65	C(6)–Mn–C(13)	95
C(3)–Mn–C(8)	105		
C(3)–Mn–C(9)	96	C(8)–Mn–C(9)	39
C(3)–Mn–C(10)	111	C(8)–Mn–C(10)	73
C(3)–Mn–C(11)	138	C(8)–Mn–C(11)	95
C(3)–Mn–C(12)	163	C(8)–Mn–C(12)	92
C(3)–Mn–C(13)	150	C(8)–Mn–C(13)	66
C(4)–Mn–C(5)	39		
C(4)–Mn–C(6)	65	C(9)–Mn–C(10)	41
C(4)–Mn–C(8)	141	C(9)–Mn–C(11)	77
C(4)–Mn–C(9)	114	C(9)–Mn–C(12)	96
C(4)–Mn–C(10)	102	C(9)–Mn–C(13)	92
C(4)–Mn–C(11)	106		
C(4)–Mn–C(12)	125	C(10)–Mn–C(11)	40
C(4)–Mn–C(13)	153	C(10)–Mn–C(12)	75
C(11)–Mn–C(12)	40	C(10)–Mn–C(13)	94
C(11)–Mn–C(13)	73	C(12)–Mn–C(13)	38

(*ii*) In the cyclopentadienyl ligand

At C(2)	107	C(5)	111
At C(3)	109	C(6)	108
At C(4)	107		

(*iii*) In the cycloheptatriene residue

At C(8)	124	C(12)	127
C(9)	125	C(13)	122
C(10)	129	C(14)	100
C(11)	124		

(*iv*) In the phenyl group

At C(15)	119	C(18)	118
C(16)	122	C(19)	121
C(17)	120	C(20)	120

TABLE 2 (*Continued*)

(*v*) Others

C(2)–C(6)–C(7)	126	C(13)–C(14)–C(15)	116
C(5)–C(6)–C(7)	126	C(14)–C(15)–C(16)	122
C(8)–C(14)–C(15)	120	C(14)–C(15)–C(20)	119

(*c*) Intermolecular contacts $\leqslant 3.7$ Å

$C(2) \cdots C(10^{II})$	3.61	$C(10) \cdots C(2^{IV})$	3.61
$C(2) \cdots C(11^{II})$	3.59	$C(11) \ldots C(2^{IV})$	3.59
$C(7) \cdots C(11^{II})$	3.62	$C(11) \cdots C(7^{IV})$	3.62
$C(7) \cdots C(16^{III})$	3.70	$C(16) \cdots C(7^{I})$	3.70

Roman numeral superscripts refer to the following equivalent positions:

I $-x, -\frac{1}{2} + y, \frac{1}{2} - z$ III $-x, \frac{1}{2} + y, \frac{1}{2} - z$
II $-1 + x, y, z$ IV $1 + x, y, z$

(*d*) Mean estimated standard deviations

Bond lengths (Å)	
Mn–C, C–C (five-membered ring)	0.02
Others	0.03
Bond angles (°)	
At Mn 1.4	
C_5 ring 1.9	others 2.1
C_6 ring 2.3	
C_7 ring 2.4	

their positions and isotropic temperature factors adjusted by block-diagonal least-squares refinement. After convergence, the data were rescaled with the structure-factor program, and the parameters optimized by least-squares refinement including an overall scale factor, an overall temperature factor, the imaginary components of anomalous dispersion, and anisotropic temperature parameters for manganese. The final weighting scheme used was $w^{\frac{1}{2}} = 1.0$ if $|F_o| \leqslant 50.0$, otherwise $w^{\frac{1}{2}} = |F_o|/50.0$. After convergence, a difference-Fourier map was computed and searched for peaks >0.5 eÅ^{-3}; six were found, three positive (0.7, 0.5, 0.5), and three negative (-0.6, -0.5, -0.5). Atomic scattering factors and the components of anomalous dispersion were taken from ref. 3. Observed and calculated structure factors, temperature factors, and a statement of the convergence of the refinement are listed in Supplementary Publication No. SUP 22181 (12 pp.).*

DISCUSSION

Table 1 gives the final atomic co-ordinates and their standard deviations derived from the final least-squares matrix. Figure 1(*a*) shows the molecule and the crystallographic numbering system used. Figure 1(*b*) is a stereopair of drawings of the molecule seen down the *b* axis. Table 2 lists interatomic distances, valency angles, and some non-bonded interactions; Table 3 gives departures of atoms from some planes fitted by least-squares to groups of atoms.

The cyclopentadienyl ring is planar within experimental error; the carbon, C(7), of the attached methyl group departs from this plane by 0.05 Å. The mean C–C distance within this ring (1.416 Å) is close to that (1.43 Å) suggested as normal for a cyclopentadienyl ligand after correction, if necessary, for libration.[4] One bond, C(5)–C(6), is noticeably longer than the other four, but there is no theoretical reason implying equality of the bond lengths.[5] The average Mn-C(C_5H_4Me) distance (2.12 Å) is unexceptional.

TABLE 3

Mean planes and departures (Å × 10^2) of atoms from the mean planes (in square brackets). Italicized atoms were not used to locate the mean plane

Plane (1): C(2)–C(6)
[C(2) 0, C(3) 1, C(4) −1, C(5) 1, C(6) 0, *Mn* −175, *C*(7) 5]

Plane (2): C(9)—C(12)
[C(9) 0, C(10) 0, C(11) 0, C(12) 0, *Mn* 132, *C*(8) −18, *C*(13) −17]

Plane (3): C(8), C(9), C(12), C(13)
[C(8) 0, C(9) 0, C(12) 0, C(13) 0, *Mn* 135, *C*(10) −15, *C*(11) −16, *C*(14) −84]

Plane (4): C(15)—C(20)
[C(15) −1, C(16) 2, C(17) 0, C(18) −2, C(19) 2, C(20) −1, *C*(14) 12]

Interplanar angles (°): (1)—(2) 6; (1)—(3) 2; (2)—(3) 8

TABLE 4

Stereographic projection of the bond vectors about Mn. The limiting radius = 100; vectors ending in the northern hemisphere or on the equator are labelled Dot, those in the southern hemisphere, Ring

Vector to:	Radius	Azimuth	
Centroid of C_5 ring	0	0	Dot
C(2)	31	0	Dot
C(3)	31	72	Dot
C(4)	32	144	Dot
C(5)	30	−144	Dot
C(6)	31	−73	Dot
C(8)	47	20	Ring
C(9)	46	70	Ring
C(10)	41	127	Ring
C(11)	42	−174	Ring
C(12)	46	−120	Ring
C(13)	48	−69	Ring

It is convenient to regard the title compound as derived from a formally neutral cycloheptatriene ligand. Such a ligand bonded to Cr[6] or Mo[7] retains the alternation of bond lengths shown in the uncomplexed ligand, but bonding to the metal flattens the conjugated system, whose atoms define two planes. In the title compound the mean Mn–C distance for the cycloheptatriene ligand (2.102 Å) agrees with that for the cyclopentadienyl ligand, but departures from the mean in the former are much greater, the extreme values differing by three standard deviations. The longest distances are those to the terminal atoms of the triene system as in the chromium and molybdenum analogues; in (1) the terminal bonds of the triene system are the shortest ones. Table 4 describes a stereographic projection of the bond vectors about Mn. The atoms of the triene system are set precisely in two planes C(8), C(9), C(12), C(13) and C(9), C(10), C(11), C(12) inclined at 8° [*cf.* 5.7 (Cr),[6]

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[3] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 73, 77, and 149.

[4] A. F. Berndt and R. E. Marsh, *Acta Cryst.*, 1963, **16**, 118; M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, 1973, **12**, 1650 and refs. therein.

[5] M. J. Bennett, M. R. Churchill, M. Gerloch, and R. Mason, *Nature*, 1964, **201**, 1318.

[6] P. E. Baikie and O. S. Mills, *J. Chem. Soc.* (*A*), 1968, 2704.

[7] J. D. Dunitz and P. Pauling, *Helv. Chim. Acta*, 1960, **43**, 2188.

6.3 (Mo),[7] and 23.2 (non-bonded, in the *p*-bromophenacyl ester of 5,5-dimethylcyclohepta-1,5,6-triene-1-carboxylic acid)[8]]. The planes through C(8), C(9), C(12), C(13) and C(8), C(13), C(14) make an angle of 59° [*cf.* 45.7 (Cr),[6] 45.8 (Mo),[7] and 52.3 (non-bonded)[8]]. The atoms of the phenyl group depart slightly from planarity, the ring being folded approximately along the line C(16) • • • C(19); C(14) lies 0.12 Å out of the best plane through the phenyl group, displaced towards C(16) and C(19).

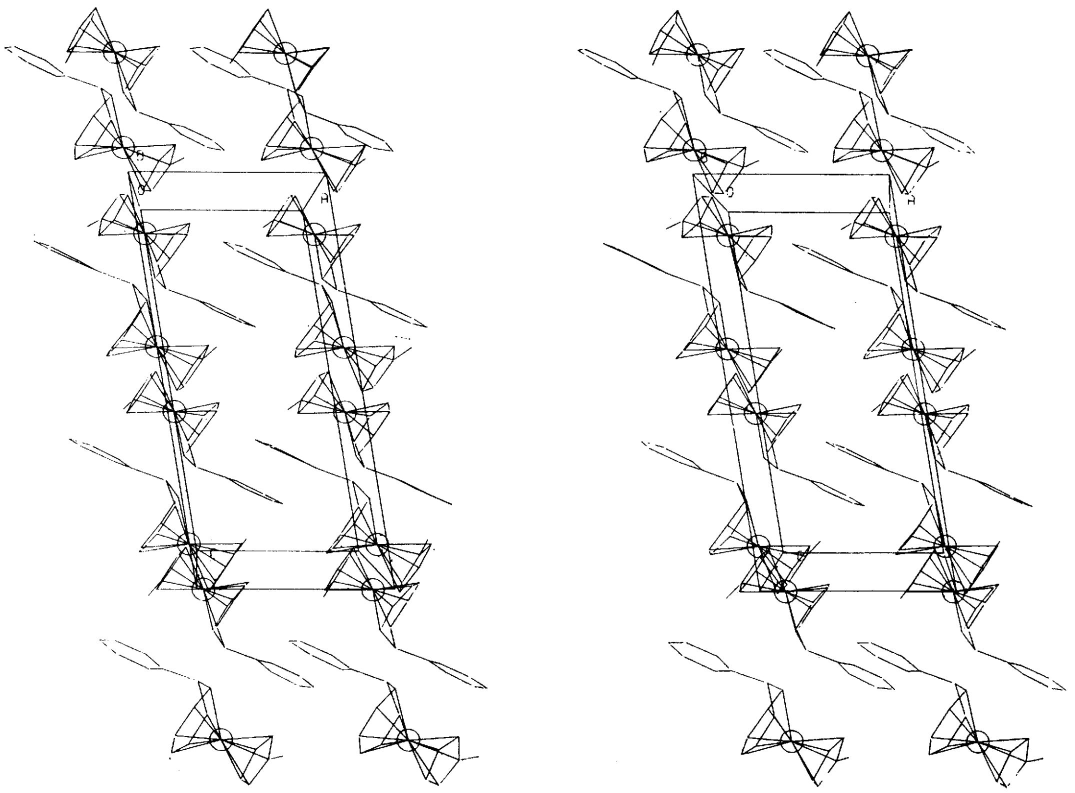

FIGURE 2 The crystal packing viewed down the *b* axis

Figure 2 is a stereopair showing the crystal structure down the *b* axis. No intermolecular contacts are unusually close. Among the four shortest ones, two involve C(7) which lies 0.05 Å from the mean plane of the cyclopentadienyl ligand; one involves C(16), one of the sites at which the phenyl group is folded; and C(11), which lies further from Mn than C(10), is involved in the closest of the intermolecular contacts. The deformations from ideality are consistent with the requirements of molecular packing.

We thank Professor Pauson and Dr. Segal for suggesting the problem and supplying crystals, and Dr. Elder and his staff at the S.R.C. Laboratory for the film-scanner data. Calculations were made on the ICL 1904 computer at the University of Strathclyde using programs of the SCXR series written by J. A. D. J.

[7/1144 *Received, 30th June*, 1977]

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[8] R. E. Davis and A. Tulinsky, *J. Amer. Chem. Soc.*, 1966, **88**, 4583.