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The Crystal and Molecular Structure of π-Cyclohexadienylmanganese Tricarbonyl

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π-Cyclohexadienylmanganese tricarbonyl, $C_6H_7Mn(CO)_3$, crystallizes in the centrosymmetric orthorhombic space group Pnma (D_{2h}^{16}; no. 62) with $a = 13.199 \pm 0.010$ Å, $b = 8.810 \pm 0.007$ Å, $c = 7.528 \pm 0.006$ Å, and $Z = 4$. Observed and calculated densities are 1.61 ± 0.04 and 1.654 g cm^{-3}, respectively. A single-crystal X-ray diffraction study of the complex has been completed using intensity data collected with a scintillation counter. All atoms (including hydrogens) have been located, the final discrepancy index being $R_F = 8.41\%$ for the 558 independent nonzero reflections. The molecules of $C_6H_7Mn(CO)_3$ are separated by normal van der Waals distances. The molecule has crystallographically required C_s symmetry and contains a π-cyclohexadienyl ligand in which the methylene group is bent away from the manganese atom by 42° 49′ relative to the planar π-dienyl system.

Introduction

It has been shown that the reaction of hydride ion with certain cationic π-cyclopentadienyl[2] and π-benzene[3] complexes of the transition metals leads to the formation of π-cyclopentadiene and π-cyclohexadienyl species, in which a noncyclic four- or five-membered delocalized system is bonded to the metal. One of the peculiarities of these systems is that complexes of unsubstituted π-cyclopentadiene or π-cyclohexadienyl ligands have an infrared absorption spectrum such that one of the methylene hydrogens is associated with a strong, broad C–H stretch at the anomalously low frequency of *ca.* 2730–2830 cm^{-1}. The molecules π-C_5H_5-$Co(C_5H_5C_6H_5)$,[4] π-$C_5H_5Co(C_5H_5COC_6H_5)$,[5] and π-C_5H_5-$Re(CH_3)_2(C_5H_5CH_3)$[6]—none of which shows this anomalous C–H stretching frequency—have each been shown crystallographically to have a substituent occupying the *exo* site on the saturated carbon atom. In keeping with this, the complex $[(CH_3)_6C_6H]Re(CO)_3$ (formed by the reaction of the hexamethylbenzenerhenium tricarbonyl cation with a hydride ion source[7]) has an intense C–H stretch at 2790 cm^{-1} and the lone nonmethyl hydrogen in this molecule has been shown crystallographically[8] to occupy the *exo* position. The structure is, however, of limited accuracy.

The present crystallographic investigation of π-cyclohexadienylmanganese tricarbonyl has been undertaken with a view of obtaining accurate data on the geometry of the π-cyclohexadienyl ligand and, if possible, to locate the hydrogen atoms of this ligand.

Unit Cell and Space Group

Crystals of $C_6H_7Mn(CO)_3$ were generously supplied by Professor R. B. King. Optical examination and preliminary X-ray diffraction photographs indicated that the crystals were orthorhombic.

Unit cell parameters, obtained from high-angle precession data taken with Mo Kα radiation on a precalibrated precession camera at 22 ± 2° are $a = 13.199 \pm 0.010$ Å, $b = 8.810 \pm 0.007$ Å, and $c = 7.528 \pm 0.006$ Å. The unit cell volume is 875.4 Å^3. The observed density (1.61 ± 0.04 g cm^{-3}, by flotation in aqueous zinc iodide solution) is in satisfactory agreement with the value calculated for $Z = 4$ ($\rho_{\mathrm{calcd}} = 1.654$ g cm^{-3} for $M = 218.09$).

A survey of $h0l$, $h1l$ Weissenberg photographs and $hk0$, $hk1$, $0kl$, $1kl$ precession photographs revealed the systematic absences $0kl$ for $k + l = 2n + 1$ and $hk0$ for $h = 2n + 1$—compatible with space group $Pn2_1a$ (no. 33) or Pnma (no. 62). The noncentrosymmetric space group $Pn2_1a$ would impose no symmetry conditions on the molecule, but the centrosymmetric space group Pnma requires (in the absence of disorder) that the molecule should possess C_s symmetry.

No piezoelectric test was performed, but the successful solution to the crystal structure (*vide infra*) showed the true space group to be the centrosymmetric Pnma (D_{2h}^{16}; no. 62), with the molecule possessing precise C_s symmetry.

Collection and Reduction of X-Ray Diffraction Data

Two crystals were used in the course of the analysis. Crystal A, a rectangular parallelepiped (0.40 × 0.08 × 0.10 mm), was mounted along its extended a direction; crystal B (0.41 × 0.26 × 0.40 mm) was mounted along its c direction. [Dimensions refer sequentially to $\vec{a}$, $\vec{b}$, $\vec{c}$.]

Intensity data were collected with a 0.01°-incrementing Buerger automated diffractometer using equiinclination Weissenberg geometry and a "stationary-background, ω-scan, stationary-background" counting sequence. The apparatus, experimental technique, and general precautions have been described at length in a previous publication.[9] Details specific to the present analysis include the following: (i) Mo Kα radiation ($\bar{\lambda}$ 0.7107 Å) was used throughout. (ii) The angle

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(1) Research Fellow of the Alfred P. Sloan Foundation, 1968–1970.

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(3) (a) G. Winkhaus and G. Wilkinson, *Proc. Chem. Soc.*, 311 (1960); (b) G. Winkhaus, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3807 (1961); (c) D. Jones and G. Wilkinson, *Chem. Ind.* (London), 1408 (1961); (d) D. Jones, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4458 (1962).

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(7) G. Winkhaus and H. Singer, *Z. Naturforsch.*, **18b**, 418 (1963).

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(9) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 1123 (1968).

scanned (ω) was chosen as $\omega = [3.0 + (1.0/L)]°$, where $1/L$ is the Lorentz factor. The count associated with this scan is $C(hkl)$. (iii) The speed of the ω scan was 2°/min. (iv) Initial and final backgrounds (B_1 and B_2) were each measured for one-fourth the time of the main scan. (v) Within a given zone, the stability of the entire configuration was monitored by remeasuring a carefully preselected check reflection after each batch of 20 reflections had been collected. No significant, *i.e.*, $\geqslant 3[C(hkl)]^{1/2}$ variations from the mean were detected. (vi) $I(hkl)$, the net intensity of the Bragg reflection hkl, was calculated as $I(hkl) = C(hkl) - 2[B_1(hkl) + B_2(hkl)]$.

A total of 876 reflections in the quadrants Hkl and $H\bar{k}l$ $[H = 0–6]$ were collected from crystal A, and 386 reflections in the quadrants hKl $[K = 0–4]$ were collected from crystal B. Within each zone, data are complete to $\sin\theta = 0.42$ except for the reflections with $\theta \leqslant 4°$, which are shielded from the counter by the backstop.

Data were assigned standard deviations according to the following scheme (where $\delta(hkl) = 3[C(hkl) + B_1(hkl) + B_2(hkl)]^{1/2}$): $I(hkl) \geqslant 1225$, $\sigma\{I(hkl)\} = 0.1[I(hkl)]$; $1225 > I(hkl) \geqslant \delta(hkl)$, $\sigma\{I(hkl)\} = 3.5[I(hkl)]^{1/2}$; $I(hkl) < \delta(hkl)$, reflection rejected. Of the 876 reflections collected from crystal A, 136 were rejected, and of the 386 reflections from crystal B, 31 were rejected. All data were corrected for Lorentz and polarization effects,[10] and absorption corrections were applied[11] ($\mu = 15.8$ cm^{-1} for Mo Kα radiation).[12] The resulting transmission coefficients ranged from 0.842 to 0.942 for data from crystal A (volume 0.0022 mm^3) and from 0.581 to 0.872 for data from crystal B (volume 0.047 mm^3). Data for the quadrants Hkl and $H\bar{k}l$ were averaged. These data are nonequivalent only if the true space group is the polar Pn2$_1$a. The 12 zones of data (0–6kl and hk0–4) were merged to a common scale using a least-squares procedure which minimizes a set of residuals linear in the logarithm of the individual scale factors.[13] [The over-all R factor for scaling was ~4.5% based on F^2.] The resulting 558 independent nonzero reflections were used in calculating a Wilson plot,[14] from which were obtained the approximate absolute scale and the over-all isotropic thermal parameter.

Elucidation and Refinement of the Structure

Two manganese coordinates ($x = 0.046$ and $z = 0.184$) were obtained by inspection of a three-dimensional Patterson synthesis[15] which had been sharpened so as to be θ independent. The remaining manganese coordinate was chosen as $y = 0.25$. It is arbitrary if the space group is Pn2$_1$a and must be $^1/_4$ for space group Pnma. A three-dimensional difference-Fourier synthesis, phased only by the manganese atom ($R_F = 0.391$),[16] showed half of the molecule to be the mirror image (reflected about $y = {}^1/_4$) of the other half, thus confirming the true space group to be Pnma. All nonhydrogen atom positions were obtained from this map. Three cycles of full-matrix least-squares refinement of individual positional and isotropic thermal parameters for all nonhydrogen atoms led to convergence at $R_F = 0.135$ and $R_{wF^2} = 0.123$.[16] Refinement was continued using anisotropic thermal parameters for all atoms save the carbon atoms of the cyclohexadienyl ligand. [Experience has shown it to be difficult to locate hydrogens attached to carbon atoms which have been allowed to refine anisotropically.] Three cycles of refinement led to convergence at $R_F = 0.106$ and $R_{wF^2} = 0.0565$. A difference-Fourier synthesis at this stage led to the location of each of the five crystallographically independent hydrogen atoms in the system, peak heights (in e$^-$/Å^3) being 0.44 for H(1), 0.62 for H(2), 0.67 for H(3), 0.55 for H(4a), and 0.37 for H(4b). [Peak heights for carbon atoms on an "observed" Fourier synthesis at this stage were ~5 e$^-$/Å^3.]

Finally, three cycles of refinement of individual positional and anisotropic thermal parameters for all nonhydrogen atoms resulted in convergence ($\Delta/\sigma < 0.05$) at $R_F = 0.0841$ and $R_{wF^2} = 0.0359$. A final difference-Fourier synthesis showed no significant features, thus validating the results of the least-squares refinement.

Throughout the analysis, the residual $\Sigma w(|F_o|^2 - |F_c|^2)^2$ was minimized, where $w = [(\mathrm{Lp})^{-1}(T^*)^{-1}\cdot\sigma\{I(hkl)\}]^{-2}$, T^* being the transmission factor for the appropriate reflection. Scattering factors for neutral manganese, oxygen, carbon and hydrogen were taken from the compilation of Ibers.[17] The contribution from the manganese atom was corrected to allow for dispersion ($\Delta f' = +0.4$ e$^-$, $\Delta f'' = +0.9$ e$^-$).[18] Hydrogen atom positions were taken from the difference-Fourier map on which they were initially located and were not refined, each hydrogen being assigned an isotropic thermal parameter of $B = 2.0$ Å^2.

Observed and calculated structure factors are shown in Table I. Final atomic positions are given in Table II. Anisotropic thermal parameters are collected in Table III; the associated atomic vibration ellipsoids are defined in Table IV.

The Molecular Structure

Intramolecular distances, the over-all molecular stereochemistry, and the system for numbering atoms are shown in Figure 1. Interatomic angles are collected in Table V. The molecule possesses exact (*i.e.*, crystallographically required) C$_s$ symmetry, the mirror plane at $y = {}^1/_4$ containing the manganese atom, one carbonyl ligand [C(5)–O(1)], and two carbon and three

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(10) $(\mathrm{Lp})^{-1} = 2\cos^2\bar{\mu}\sin\Upsilon/(1 + \cos^2 2\theta)$ where $\bar{\mu}$ is the equiinclination angle, Υ is the vertical Weissenberg coordinate, and θ is the Bragg angle.

(11) Using a local modification of GNABS—a FORTRAN general absorption correction program by C. W. Burnham.

(12) "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, pp 162–163.

(13) A. D. Rae, *Acta Cryst.*, **19**, 683 (1965).

(14) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

(15) All crystallographic computations (including Fourier syntheses, structure factor calculations, least-squares refinement, distance–angle–plane calculations) were performed using the CRYM system—an integrated package of crystallographic routines for the IBM 7094 computer, compiled under the direction of Professor R. E. Marsh of the California Institute of Technology.

(16) $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_{wF^2} = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$.

(17) "International Tables for X-ray Crystallography," Volume 3, The Kynoch Press, Birmingham, England, 1962, pp 202–203, 211–212.

(18) See ref 17, p 216.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS (IN ELECTRONS × 10.00) FOR $C_6H_7Mn(CO)_3$

K	L	FO	FC
H = 0			
0	2	966	957
0	4	94	71
0	6	362	339
0	8	229	203
1	3	494	453
1	5	59	74
1	7	174	169
2	0	745	965
2	2	185	179
2	4	80	90
2	6	323	333
2	8	228	199
3	1	148	107
3	3	242	203
3	5	364	357
3	7	210	211
4	0	923	920
4	2	180	190
4	4	285	251
4	6	481	492
4	8	145	149
5	1	379	388
5	3	178	159
5	5	292	263
5	7	185	137
6	0	756	746
6	2	258	247
6	4	104	111
6	6	172	142
7	1	423	404
7	3	235	227
7	5	63	28
8	0	653	634
8	2	198	178
8	4	53	54
9	1	182	191
9	3	102	62
10	0	199	146
10	2	65	20
H = 1			
0	2	485	494
0	3	101	121
0	4	105	116
0	5	324	344
0	6	99	84
0	7	88	80
0	8	72	91
1	2	155	163
1	3	96	73
1	4	295	334
1	5	113	101
1	6	185	198
1	7	125	108
1	8	59	30
2	1	821	788
2	2	205	177
2	3	877	862
2	4	112	115
2	5	439	460
2	7	79	35
2	8	69	56
3	1	170	155
3	2	319	317
3	3	56	48
3	4	562	569
3	5	115	114
3	6	199	216
3	8	62	78
4	1	226	226
4	2	51	25
4	3	371	382
4	4	251	234
4	5	429	436
4	7	102	110
5	1	55	60
5	2	88	97
5	3	49	51
5	4	358	349
5	5	96	91
5	6	180	182
5	7	75	25
6	1	313	317
6	2	39	39
6	3	347	347
6	4	88	74
6	5	244	234
6	6	89	52
6	7	43	16
7	1	110	95
7	2	196	192
7	3	32	29
7	4	170	165
7	5	73	59
7	6	76	61
8	1	152	159
8	2	75	75
8	3	107	117
8	4	90	37
8	5	129	132
9	1	71	54
9	2	81	62
9	4	138	133
10	1	109	93
10	2	61	11
H = 2			
0	2	772	762
0	3	131	134
0	4	102	88
0	5	86	81
0	6	350	304
0	7	114	105
0	8	171	168
1	1	489	480
1	2	211	207
1	3	303	310
1	4	100	90
1	5	85	87
1	6	70	56
1	7	211	199
1	8	108	104
2	0	568	562
2	1	839	833
2	2	390	377
2	3	71	47
2	4	67	64
2	5	328	330
2	6	186	188
2	7	192	158
2	8	168	165
3	0	198	209
3	1	348	315
3	2	260	254
3	3	112	114
3	4	79	95
3	6	210	210
3	7	166	158
3	8	106	90
4	0	721	706
4	1	112	108
4	2	291	299
4	3	168	170
4	4	70	59
4	5	178	184
4	6	161	151
4	7	130	129
4	8	109	124
5	0	68	67
5	1	361	350
5	2	134	144
5	3	100	106
5	5	93	23
5	6	93	105
5	7	121	123
6	0	358	348
6	1	361	364
6	2	247	263
6	4	56	40
6	5	126	110
6	6	122	126
6	7	57	83
7	0	345	337
7	1	210	198
7	2	107	97
7	3	149	148
7	4	34	5
7	5	94	41
7	6	46	22
8	0	237	225
8	1	170	170
8	2	173	177
8	4	54	16
8	5	49	0
9	1	134	128
9	2	102	51
9	3	91	39
10	0	123	130
10	1	114	77
10	2	126	64
H = 3			
0	2	1107	1107
0	3	582	563
0	4	594	624
0	5	291	301
0	6	192	186
0	7	84	100
0	8	99	59
1	2	262	272
1	3	481	476
1	4	362	408
1	6	94	75
1	7	134	113
1	8	87	60
2	1	430	453
2	2	244	226
2	3	417	415
2	4	212	246
2	5	300	308
2	6	204	212
2	7	75	29
2	8	61	27
3	1	148	127
3	2	526	516
3	3	238	226
3	4	287	272
3	5	171	168
3	6	203	225
3	7	62	75
3	8	48	13
4	1	455	448
4	2	579	567
4	3	414	399
4	4	326	337
4	5	260	265
4	6	65	88
4	7	76	85
4	8	39	81
5	1	73	68
5	2	324	303
5	3	319	315
5	4	223	205
5	5	99	125
5	6	109	114
5	7	49	43
6	1	119	121
6	2	192	197
6	3	206	199
6	4	189	185
6	5	161	144
6	6	155	140
6	7	63	39
7	1	70	21
7	2	63	66
7	3	174	142
7	4	178	149
7	5	143	140
7	6	51	19
8	1	47	38
8	2	210	206
8	3	137	162
8	4	184	169
8	5	137	125
9	1	73	28
9	2	103	105
9	3	151	145
9	4	140	127
10	1	73	91
H = 4			
0	0	155	161
0	1	221	191
0	2	144	139
0	3	114	74
0	4	237	193
0	5	248	197
0	6	145	117
0	7	260	251
0	8	124	74
1	0	497	424
1	1	241	231
1	2	293	274
1	3	232	233
1	4	66	41
1	5	88	120
1	6	166	158
1	7	74	61
1	8	161	157
2	1	976	1019
2	0	743	757
2	1	949	1019
2	2	102	105
2	3	93	90
2	4	66	14
2	5	174	150
2	6	160	165
2	7	245	227
2	8	74	74
3	0	704	719
3	1	267	262
3	2	545	532
3	3	51	19
3	4	127	134
3	5	94	87
3	6	51	12
3	7	69	53
3	8	158	145
4	0	245	264
4	1	638	649
4	2	81	54
4	3	208	210
4	4	119	95
4	5	157	133
4	7	156	150
5	0	205	205
5	1	103	112
5	2	296	294
5	3	93	89
5	4	92	95
5	5	73	30
5	6	56	25
5	7	44	43
6	0	295	305
6	1	309	314
6	2	102	91
6	3	50	23
6	4	69	42
6	5	155	133
6	6	111	107
7	0	36	18
7	1	132	148
7	2	117	125
7	3	90	89
7	4	99	88
7	5	75	93
7	6	109	118
8	0	114	120
8	1	93	90
8	2	59	40
8	3	44	32
8	4	84	37
8	5	49	73
9	0	79	92
9	1	54	43
9	2	146	131
10	0	117	110
H = 5			
0	1	460	444
0	2	722	713
0	3	80	63
0	4	749	789
0	5	95	70
0	6	192	192
0	7	61	2
0	8	71	8
1	1	95	86
1	2	63	67
1	3	530	535
1	4	75	80
1	5	359	386
1	6	59	11
1	7	84	89
2	1	54	62
2	2	491	470
2	3	254	233
2	4	416	438
2	5	96	106
2	6	175	191
2	7	97	69
2	8	68	34
3	1	236	228
3	2	98	107
3	3	272	268
3	4	166	157
3	5	182	198
3	6	38	16
3	7	71	66
3	8	75	52
4	1	140	138
4	2	523	528
4	3	103	91
4	4	295	283
4	5	138	133
4	6	119	108
5	1	192	140
5	2	74	77
5	3	286	261
5	4	139	134
5	5	176	172
5	7	88	52
6	1	77	46
6	2	242	242
6	3	69	86
6	4	304	305
6	6	124	129
7	1	49	27
7	2	37	20
7	3	251	244
7	4	45	18
7	5	197	210
8	1	81	90
8	2	183	185
8	4	251	251
9	1	45	50
9	2	88	34
9	3	165	142
H = 6			
0	0	284	267
0	1	567	577
0	2	83	77
0	3	111	116
0	4	288	280
0	5	295	243
0	6	132	154
0	7	200	205
0	8	90	4
1	0	516	464
1	1	297	282
1	2	278	297
1	4	25	29
1	6	201	174
1	8	154	146
2	0	209	203
2	1	599	608
2	3	205	194
2	4	114	112
2	5	156	160
2	6	73	78
2	7	204	184
3	0	593	549
3	1	79	83
3	2	368	384
3	3	91	85
3	4	56	57
3	5	206	225
3	6	147	141
3	7	73	37
4	0	402	388
4	1	548	573
4	2	152	149
4	3	193	197
4	4	58	4
4	5	165	148
4	7	195	185
5	0	387	384
5	1	57	62
5	2	249	244
5	3	66	16
5	5	99	63
5	6	140	141
5	7	111	15
6	0	163	168
6	1	272	270
6	2	27	19
6	3	72	61
6	5	130	125
6	6	75	7
7	0	172	166
7	1	153	160
7	2	103	109
7	3	40	20
7	4	60	13
8	0	90	77
8	3	64	67
8	4	52	54
9	0	190	178
H = 7			
0	1	121	88
0	2	320	332
0	3	157	117
0	4	270	251
1	1	170	157
1	2	47	37
1	3	349	341
1	4	118	127
2	1	247	228
2	3	276	283
2	4	355	352
3	2	87	92
3	3	303	288
4	1	55	68
4	2	59	57
4	3	78	63
5	1	44	17
5	3	201	197
5	4	47	51
6	1	84	75
6	2	225	246
6	3	160	140
7	1	143	122
7	2	38	22
H = 8			
0	0	762	713
0	1	602	578
0	2	317	318
0	3	63	59
0	4	53	51
1	0	415	384
1	3	118	100
1	4	94	86
2	0	312	280
2	1	222	229
2	2	176	209
2	3	128	131
3	0	144	151
3	1	66	72
3	2	337	353
3	3	48	50
4	0	233	196
4	1	369	386
4	2	145	133
4	3	115	126
4	4	124	125
5	0	219	229
5	1	99	98
5	2	243	250
5	3	33	34
5	4	85	83
6	0	201	203
6	1	152	159
6	2	115	137
7	0	130	119
7	1	153	159
H = 9			
0	1	227	194
0	2	117	102
0	3	265	239
0	4	176	174
1	1	76	98
1	2	177	156
1	3	324	287
1	4	47	72
2	2	301	297
2	3	266	257
3	1	73	61
3	2	44	48
3	3	246	235
3	4	203	204
4	2	66	57
4	3	268	280
4	4	88	72
5	2	96	98
5	3	158	153
6	1	68	56
6	2	145	162
H = 10			
0	0	408	354
0	1	98	74
0	2	278	236
0	3	73	47
1	1	313	287
1	2	51	47
1	3	91	99
2	0	335	342
2	1	68	54
2	2	252	246
2	3	88	89
3	0	246	263
3	2	157	178
3	4	85	75
4	0	114	95
4	2	150	148
4	3	42	63
5	0	157	137
5	2	88	87
H = 11			
0	1	151	140
0	2	74	36
0	3	316	297
1	1	92	25
1	2	187	169
1	3	108	127
2	1	98	93
2	3	209	186
3	1	36	52
3	2	208	202
3	3	32	39
4	1	174	185
H = 12			
0	0	177	77
0	1	65	51
0	2	155	184
1	0	36	19
1	1	179	169
1	2	39	37
1	3	127	119
2	0	329	302
2	1	47	1
2	2	147	148
2	2	147	148

TABLE II

FINAL ATOMIC COORDINATES (WITH ESD'S) FOR $C_6H_7Mn(CO)_3$[a,b]

Atom	x	y	z
Mn	0.54312 (12)	0.25000 (–)[c]	0.31260 (20)
O(1)	0.4399 (7)	0.2500 (–)[c]	0.6592 (13)
O(2)	0.4117 (6)	0.4821 (7)	0.1492 (8)
C(1)	0.6787 (9)	0.2500 (–)[c]	0.1562 (13)
C(2)	0.6731 (6)	0.3881 (9)	0.2517 (13)
C(3)	0.6663 (5)	0.3853 (8)	0.4357 (12)
C(4)	0.7103 (12)	0.2500 (–)[c]	0.5322 (16)
C(5)	0.4783 (9)	0.2500 (–)[c]	0.5201 (18)
C(6)	0.4638 (6)	0.3936 (11)	0.2153 (11)
H(1)	0.6777	0.2500[c]	0.0155
H(2)	0.6724	0.4938	0.1875
H(3)	0.6650	0.4925	0.4825
H(4a)	0.7650	0.2500[c]	0.5325
H(4b)	0.6875	0.2500[c]	0.6600

[a] Esd's appear in parentheses after each parameter. They are right-adjusted to the least significant digit of the preceding number. [b] Only atoms of the asymmetric unit are listed. Atoms in the other half of the molecule are related to these by the transformation: $x' = x$, $y' = 1/2 - y$, $z' = z$. [c] Coordinate crystallographically required to be precisely $y = 1/4$.

TABLE III

ANISOTROPIC THERMAL PARAMETERS FOR $C_6H_7Mn(CO)_3$, WITH ESD'S[a,b]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Mn	48.0 (1.7)	92.8 (2.5)	111.9 (3.9)	0[c]	−1.7 (2.9)	0[c]
O(1)	84 (8)	140 (14)	197 (22)	0[c]	73 (20)	0[c]
O(2)	62 (5)	165 (10)	257 (16)	50 (12)	57 (13)	113 (21)
C(1)	52 (9)	172 (19)	79 (22)	0[c]	−14 (21)	0[c]
C(2)	51 (6)	124 (12)	181 (18)	−36 (15)	36 (18)	100 (26)
C(3)	44 (5)	108 (10)	176 (17)	0 (12)	−10 (16)	−17 (23)
C(4)	124 (13)	92 (15)	159 (26)	0[c]	−93 (33)	0[c]
C(5)	46 (8)	82 (13)	207 (29)	0[c]	−13 (26)	0[c]
C(6)	41 (6)	130 (12)	150 (17)	−2 (14)	56 (16)	11 (25)

[a] The anisotropic thermal parameter (T) is defined as $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}hk)]$. [b] Esd's are shown in parentheses. [c] Required to be zero by space group symmetry.

hydrogen atoms of the π-cyclohexadienyl ligand [*i.e.*, C(1), C(4), H(1), H(4a), H(4b)].

As anticipated, the molecule consists of an $Mn(CO)_3$ group that is bonded directly to all five unsaturated carbon atoms of a cyclohexadienyl system *via* a noncyclic π-dienyl→metal linkage. In accordance with the observed[3] diamagnetism of the complex, the formally d^6 Mn(I) ion is in a pseudooctahedral environment and achieves the appropriate rare gas configuration (*i.e.*, that of Kr) by the donation of six electrons from the π-dienyl anion[19] and two electrons from each of the three carbonyl ligands. Contacts between molecules are of the normal van der Waals type. (Packing of molecules is illustrated in Figure 2.)

The Cyclohexadienyl Ligand.—The bonding of an $Mn(CO)_3$ group to the cyclohexadienyl ligand results in the latter taking up a distinctly nonplanar configuration. The atoms C(3)–C(2)–C(1)–C(2′)–C(3′), which are bonded directly to the $Mn(CO)_3$ moiety, are coplanar (having a root-mean-square deviation of only 0.008 Å) as are their attached hydrogen atoms; see Table VI. The methylene carbon C(4) lies 0.635 Å above this plane and the π-cyclohexadienyl ligand bends across the C(3)···C(3′) axis such that the plane defined by C(3)–C(4)–C(3′) makes a dihedral angle of 42° 49′ with the planar five-membered dienyl system.

Carbon–carbon distances around the delocalized system average 1.401 ± 0.014 Å; none differs significantly from this mean value. In the noncyclic π-

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[19] Consideration of π-cyclopentadienyl and π-dienyl systems as formal six-electron anionic donors is, of course, only one of the possible conventions. It is equally satisfactory to consider the complex as a d^7 Mn(0) derivative with five electrons donated from a π-dienyl radical.

TABLE IV

ATOMIC VIBRATION ELLIPSOIDS[a]

Atom	B_{maj}, Å²	B_{med}, Å²	B_{min}, Å²
Mn	3.34	2.88	2.53
O(1)	6.75	4.35	3.54
O(2)	7.02	5.73	2.47
C(1)	5.34	3.68	1.74
C(2)	5.31	4.30	1.91
C(3)	4.08	3.29	3.01
C(4)	9.25	2.99	2.86
C(5)	4.73	3.17	2.53
C(6)	4.31	4.00	1.99

[a] The major, median, and minor axes of the atomic vibration ellipsoids are defined in terms of the isotropic thermal parameter, B. The transformation to root-mean-square displacement, $(\overline{U^2})^{1/2}$, is: $(\overline{U^2})^{1/2} = (B/8\pi^2)^{1/2}$.

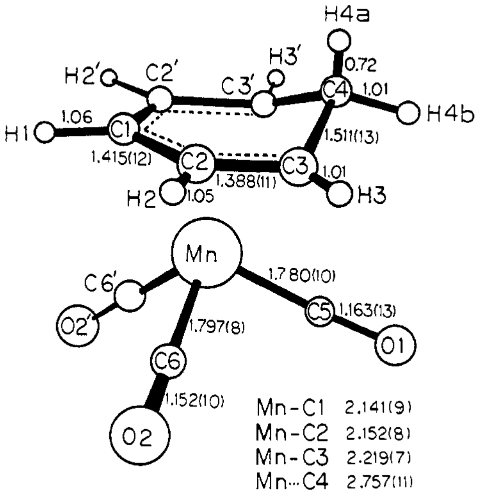

Figure 1.—Intramolecular distances, the molecular stereochemistry, and numbering of atoms in $C_6H_7Mn(CO)_3$. [Estimated standard deviations of bond lengths are shown in parentheses; these are right-adjusted to the last digit of the preceding number. Since hydrogen atom positions are taken from a difference-Fourier synthesis (see text), no precise esd's on carbon-hydrogen bond lengths are available; however, they are probably *ca.* 0.1 Å.]

TABLE V

INTERATOMIC ANGLES (WITH ESD'S) FOR $C_6H_7Mn(CO)_3$

Atoms	Angle, deg	Atoms	Angle, deg
(a) Angles around Manganese Atom			
C(1)–Mn–C(2)	38.5 (3)	C(5)–Mn–C(6)	94.5 (0.4)
C(2)–Mn–C(3)	37.0 (3)	C(6)–Mn–C(6′)	89.4 (0.4)
C(3)–Mn–C(4)	33.2 (3)	O(1)···Mn···O(2)	95.6 (0.2)
		O(2)···Mn···O(2′)	87.7 (0.2)
(b) Angles within Cyclohexadienyl Ring			
C(2)–C(1)–C(2′)	118.6 (8)	C(2)–C(3)–C(4)	117.9 (8)
C(1)–C(2)–C(3)	119.7 (8)	C(3)–C(4)–C(3′)	104.1 (8)
(c) Angles Involving Hydrogen Atoms[a]			
H(1)–C(1)–C(2)	120	H(3)–C(3)–C(4)	125
C(1)–C(2)–H(2)	122	C(3)–C(4)–H(4a)	112
H(2)–C(2)–C(3)	118	C(3)–C(4)–H(4b)	110
C(2)–C(3)–H(3)	109	H(4a)–C(4)–H(4b)	107
(d) Angles within Carbonyl Groups			
Mn–C(5)–O(1)	177.2 (9)	Mn–C(6)–O(2)	177.7 (8)

[a] Hydrogen atom positions are from a difference-Fourier map. Therefore no esd's on these angles are available.

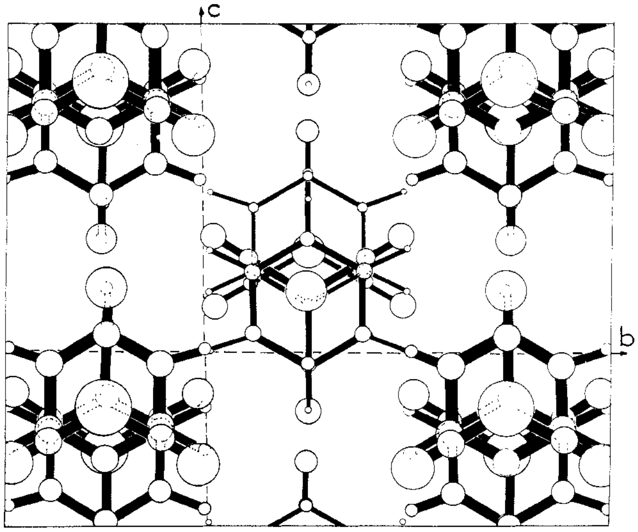

Figure 2.—Packing diagram for the $C_6H_7Mn(CO)_3$ crystal, viewed down a.

TABLE VI

SOME IMPORTANT LEAST-SQUARES PLANES WITHIN THE $C_6H_7Mn(CO)_3$ MOLECULE[a,b]

(a) $0.9973X + 0.0000Y + 0.0730Z = 9.0075$

Atom	Dev, Å	Atom	Dev, Å
C(1)*	+0.012	C(4)	+0.635
C(2)*	−0.009	H(1)	−0.08
C(3)*	+0.003	H(2)	−0.05
C(3′)*	+0.003	H(3)	+0.01
C(2′)*	−0.009	H(4a)	+1.36
Mn	−1.686	H(4b)	+0.41
O(1)	−2.854	C(5)	−2.425
O(2)	−3.506	C(6)	−2.783
O(2′)	−3.506	C(6′)	−2.783

(b) C(3)-C(4)-C(3′) Plane:

$-0.7812X + 0.0000Y + 0.6242Z = -4.8229$

(c) C(5)-C(6)-C(6′) Plane:

$-0.9965X + 0.000Y + 0.0831Z = -5.9659$

[a] The equation of each plane is expressed in Cartesian coordinates—*i.e.*, $X = xa$, $Y = yb$, $Z = zc$. [b] Planes are calculated using unit weights for each atom marked with an asterisk.

dienyl systems which have been studied previously, carbon–carbon bond lengths average 1.403 Å (for guaiazulenedimolybdenum hexacarbonyl[20]) and 1.417 Å (for azulenedimanganese hexacarbonyl[21]). In each case the mean carbon–carbon bond length is less than the established value of ~1.43 Å for the C–C distance in π-cyclopentadienyl systems, indicating that carbon–carbon bonds in a complexed π-dienyl system are stronger than those in the corresponding π-cyclopentadienyl case. [In keeping with this, it is found that the metal→π-dienyl linkage is weaker than the metal→π-cyclopentadienyl linkage; *vide infra.*]

The bonds linking the methylene group [H(4a)–C(4)–H(4b)] to the π-dienyl system—*i.e.*, C(3)–C(4) and C(3′)–C(4)—are each 1.511 ± 0.013 Å in length and are

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(20) M. R. Churchill and P. H. Bird, *Inorg. Chem.*, **7**, 1545 (1968).

(21) M. R. Churchill and P. H. Bird, *ibid.*, **7**, 1793 (1968).

thus in agreement with the recognized C(sp^2)–C(sp^3) single-bond distance of 1.510 ± 0.005 Å.[22]

Angles within the cyclohexadienyl ring are each slightly less than the ideal sp^2 or sp^3 value; the largest discrepancy is for the internal angle of the methylene group [*i.e.*, ∠C(3)–C(4)–C(3′)], which, at 104.1 ± 0.8°, is some 6.7σ lower than the ideal tetrahedral angle of 109.5°. A similar but more pronounced decrease is observed for cyclopentadiene complexes; thus, the internal C–C–C angle at the methylene atom in π-C_5H_5-$CoC_5H_5C_6H_5$ is 93.9 ± 1.5°.[4] In each case it is probable that the decrease occurs in order to maximize the overlap of the metal orbitals with the terminal atoms of the delocalized system (*i.e.*, C(3) and C(3′) in the present case).

Manganese–carbon distances vary systematically and symmetrically around the π-dienyl system in $C_6H_7Mn(CO)_3$. The central atom of the dienyl system [C(1)] is only 2.141 ± 0.009 Å from the manganese ion, the intermediate carbon atoms [C(2) and C(2′)] are each 2.152 ± 0.008 Å from the manganese, and the terminal atoms [C(3) and C(3′)] are each 2.219 ± 0.007 Å from the metal. [The methylene carbon—C(4)—is more than 0.5 Å further distant from the manganese, the Mn···C(4) contact being 2.757 ± 0.011 Å.] It should be noted that a similar lack of equivalence of metal–carbon distances has been observed in previously examined noncyclic π-dienyl systems. Thus, in the π-dienyl system of guaiazulenedimolybdenum hexacarbonyl,[20] Mo–C distances range from 2.268 ± 0.017 Å (central atom) to 2.460 Å (average) for the terminal carbon atoms. In azulenedimanganese hexacarbonyl[21] the corresponding Mn–C distances are 2.123 ± 0.010 Å for the central carbon atom and 2.279 Å (average) for the terminal carbons.

As might be expected, the mean Mn–C distance of 2.177 Å in the present complex, like the mean Mn–C distance of 2.191 Å for atoms of the π-dienyl system of $C_{10}H_8Mn_2(CO)_6$,[21] is greater than the corresponding metal–carbon distances in cyclically delocalized π-cyclopentadienyl species—*viz.*, Mn–C(π-C_5H_5) = 2.151 Å (average) for π-$C_5H_5Mn(CO)_3$[23] and 2.169 Å (average) for the π-cyclopentadienyl system in $C_{10}H_8Mn_2(CO)_6$.[21] This may be interpreted in terms of metal→π-cyclopentadienyl bonding being stronger than metal→π-dienyl bonding and is consistent with differences in carbon–carbon bond lengths within the two systems (*vide supra*).

The hydrogen atoms of the π-cyclohexadienyl ligand have each been located, albeit only by difference-Fourier methods. Individual carbon–hydrogen distances range from 0.72 to 1.06 Å, the mean of the seven bond lengths being 0.99 Å. Although this distance is shorter than the spectroscopically determined value of 1.084 ± 0.005 Å for an aromatic carbon–hydrogen bond,[24] it is now well established that light atom–hydrogen distances obtained by X-ray diffraction techniques are systematically shorter than those determined from spectroscopic or neutron diffraction studies.[25–28]

The Mn(CO)$_3$ Group.—The relative orientation of the π-cyclohexadienyl ligand and the Mn(CO)$_3$ group is illustrated in Figure 3. One carbonyl ligand [C(5)–O(1)] lies in the crystallographic mirror plane at $y = {}^1/_4$ and is directly below C(4) such that C(4)···C(5) = 3.062 ± 0.015 Å. The remaining carbonyl groups, C(6)–O(2) and C(6′)–O(2′) pass almost immediately below C(2) and C(2′) such that C(2)···C(6) = 2.775 ± 0.011 Å, while C(1)···C(6) = 3.136 ± 0.012 Å and C(3)···C(6) = 3.146 ± 0.011 Å.

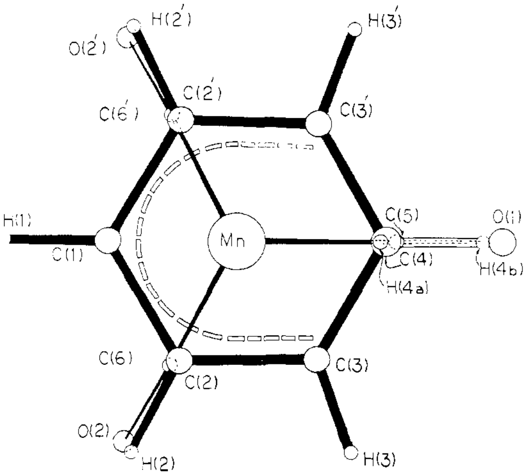

Figure 3.—The $C_6H_7Mn(CO)_3$ molecule projected on 100.

The average manganese–carbon and carbon–oxygen distances in the present structure are 1.789 ± 0.009 and 1.158 ± 0.012 Å, respectively. These may be compared to the mean values in other complexes containing Mn(CO)$_3$ groups—*viz.*, Mn–C = 1.797 Å, C–O = 1.134 Å in π-$C_5H_5Mn(CO)_3$; Mn–C = 1.803 Å, C–O = 1.151 Å in $C_{10}H_8Mn_2(CO)_6$.[21] The carbonyl ligands, with Mn–C(5)–O(1) = 177.2 ± 0.9° and Mn–C(6)–O(2) = Mn–C(6′)–O(2′) = 177.7 ± 0.8° are only slightly, but nonetheless significantly, distorted from the ideal linear configuration. Such distortions are expected as the result of unequal population of the two π^*-antibonding orbitals on the carbonyl ligands, which Kettle[29] has shown will occur for M(CO)$_3$ groups in environments having lower than C_3 symmetry. Further results of the π-cyclohexadienyl ligand having only C_s symmetry follow. (i) the OC–Mn–CO angles become nonequivalent and have only C_s symmetry. The two (symmetry-related) angles C(5)–Mn–C(6) and C(5)–Mn–C(6′) have values of 94.5 ± 0.4°, while the remaining angle, C(6)–Mn–C(6′), is only 89.4 ± 0.4°. This difference of 5.1° represents almost 13σ and is definitely

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[22] "Tables of Interatomic Distances and Configuration in Molecules and Ions; Supplement 1956–1959," Special Publication No. 18, The Chemical Society, London, 1965, p S15s.

[23] A. F. Berndt and R. E. Marsh, *Acta Cryst.*, **16**, 118 (1963).

[24] See ref 22, p S18s.

[25] (a) W. N. Lipscomb, *J. Chem. Phys.*, **22**, 985 (1954); (b) W. Smith and W. N. Lipscomb, *ibid.*, **43**, 1060 (1965).

[26] A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, **6**, 1911 (1967), especially Table III.

[27] D. Bright and J. A. Ibers, *ibid.*, **7**, 1099 (1968), especially p 1103.

[28] W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, Inc., New York, N. Y., 1968.

[29] S. F. A. Kettle, *Inorg. Chem.*, **4**, 1661 (1965).

significant. (ii) The plane defined by the carbon atoms of the carbonyl ligands is not parallel to the π-dienyl plane but, rather makes an angle of 9° 00′ with this system, with the ligand C(5)–O(1) being displaced toward C(4). The angle between the noncyclic π-dienyl system and the associated carbonyl carbon atoms in $C_{10}H_8Mn_2(CO)_6$ is 11° 42′.[21] In other noncyclic systems this angle may be even greater. In $(C_{10}H_8)_2Fe_4(CO)_{10}$ there is a dihedral angle of 17° between a *cis*-1,3-diene system and the plane of the carbonyl carbons,[30] and in $C_6F_8Fe(CO)_3$ this angle reaches 21°.[31]

Discussion

The present crystallographic analysis has succeeded in its primary objectives of determining accurately the conformation of the π-cyclohexadienyl ligand and locating (although only approximately) the hydrogen atoms in the $C_6H_7Mn(CO)_3$ molecule. It is found that the stereochemistry of the π-cyclohexadienyl methylene group is fairly regular, although the internal C–C–C angle is some 5.5° lower than the ideal sp^3 value. The structural analysis does not, however, give any unambiguous information on the cause of the anomalous C–H stretch [which is firmly established as being associated with the *exo* hydrogen of the methylene group (see Introduction)]. Possible causes of this phenomenon bear some further consideration.

It is established that the cyclopentadiene molecule has a normal infrared absorption spectrum and that only when this ligand becomes complexed to a metal atom is an anomalous C–H stretch observed. We therefore infer that, in the π-cyclohexadienyl system also, the anomalous C–H stretch is related *in some way* to the ligand being bonded to a transition metal. Two distinct possibilities arise. (1) The anomalous C–H stretch results from some metal-to-ligand interaction which directly affects the methylene group in some way—*e.g.*, direct electronic interaction between the metal atom and the carbon of the methylene group. (2) The $C-H_{exo}$ stretch is not due to the interaction of the metal atom with the methylene group but is caused simply by the stereochemical conformation which the π-cyclohexadienyl ligand is forced to adopt in order to bond satisfactorily to a transition metal ion.

A consideration of the available data[3,7,32–34] [see Table VII] shows no distinct relationships between the nature of the metal and the observed $C-H_{exo}$ stretching frequency. It seems significant, however, that the only nonsubstituted π-cyclohexadienyl complex for which a $C-H_{exo}$ stretch is *not* observed is the positively charged species $C_6H_7Fe(CO)_3^+$ in which the d orbitals would be contracted relative to neutral first-row transition metal complexes. This would tend to put some additional weight to explanation (1), but it should be remembered that negative infrared evidence is often inconclusive.

TABLE VII
INFRARED FREQUENCIES FOR THE ANOMALOUS C–H STRETCH IN SOME π-CYCLOHEXADIENYL COMPLEXES

Complex	(C–H), cm^{-1}	Ref
$C_6H_7V(CO)_4$	2795 vs (C_6D_6)	32
	2822 vs (KBr)	32
1,3,5-$(CH_3)_3C_6H_4V(CO)_4{}^a$	2790 vs (KBr)	32
1,2,4,5-$(CH_3)_4C_6H_3V(CO)_4{}^a$	2770 vs (acetone-d_6)	32
	2800 vs (KBr)	32
$C_6H_7Mn(CO)_3$	2830 s (CCl_4)	3b
$CH_3C_6H_6Mn(CO)_3{}^b$	2809 s (CCl_4)	3b
$C_6H_7Mn[C_6(CH_3)_6]$	2730 s (KBr)	33
$C_6H_7Fe(CO)_3{}^+BF_4{}^-$	No identifiable band	3d
$(C_6H_7)_2Ru$	2772 s (CCl_4)	3d
$C_6H_7ReC_6H_6$	2750 vs (CCl_4)	3d
$[C_6(CH_3)_6H]Re[C_6(CH_3)_6]^c$	2779 m (KBr)	34
$[C_6(CH_3)_6H]Re(CO)_3{}^c$	2790 (KBr)	7
$C_6H_7V(CO)$-$d_1{}^d$	2070 (KBr)	32
$C_6H_4(CH_3)_3V(CO)_4$-$d_1{}^d$	2080 (KBr)	32
$C_6H_7Mn(CO)_3$-$d_1{}^d$	2120 (CCl_4)	3b

[a] Methyl group occupying the 1-*endo* position. [b] Mixture of isomers but methyl group not in the 1-*exo* position. [c] Hydrogen in the 1-*exo* position. [d] Deuterium occupies the 1-*exo* position.

In summary, it is apparent that further data are necessary before an unambiguous explanation of the $C-H_{exo}$ stretch is forthcoming.

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(30) M. R. Churchill and P. H. Bird, *J. Am. Chem. Soc.*, **90**, 3241 (1968); M. R. Churchill and P. H. Bird, *Inorg. Chem.* **8**, 1941 (1969).

(31) M. R. Churchill and R. Mason, *Proc. Chem. Soc.*, 226 (1964); M. R. Churchill and R. Mason, *Proc. Roy. Soc.* (London), **A301**, 433 (1967).

(32) F. Calderazzo, *Inorg. Chem.*, **5**, 429 (1966).

(33) E. O. Fischer and M. W. Schmidt, *Chem. Ber.*, **100**, 3782 (1967).

(34) E. O. Fischer and M. W. Schmidt, *ibid.*, **99**, 2206 (1966).