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IOWA STATE UNIVERSITY, AMES, IOWA 50010

The Crystal Structure of Dicarbonyl-π-cyclopentadienylbicyclo[2.2.1]hepta-2π,5-dienemanganese(I)[1a,b]

BY BARRY GRANOFF AND ROBERT A. JACOBSON

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The structure of dicarbonyl-π-cyclopentadienylbicyclo[2.2.1]hepta-2π,5-dienemanganese(I), $(C_5H_5)Mn(C_7H_8)(CO)_2$, has been determined by means of a three-dimensional single-crystal X-ray investigation. The compound crystallizes in the monoclinic system with space group $P2_1/m$ in a unit cell of dimensions: $a = 6.19 \pm 0.02$, $b = 11.16 \pm 0.02$, $c = 8.98 \pm 0.02$ Å, and $\beta = 98.50 \pm 0.7°$. The calculated density of 1.61 g/cm^3, for two molecules in the unit cell, agrees quite well with the observed density of 1.57 g/cm^3 which was determined by means of the flotation method. Anisotropic full-matrix least-squares refinement has yielded a final discrepancy factor of $R = 9.1\%$ for 1550 observed reflections. The crystal consists of discrete molecules of $(C_5H_5)Mn(C_7H_8)(CO)_2$, and, although the point symmetry is C_s, the coordination about the central Mn atom is distorted tetrahedral. The manganese atom is bonded to the norbornadiene moiety in an *exo* configuration; one double bond of the olefin is not coordinated. The Mn–C(carbonyl) distance is 1.794 ± 0.007 Å and the Mn–C–O angle is 177.8 ± 0.7°. The distance from the manganese atom to the center of the cyclopentadienyl ring is 1.805 ± 0.009 Å, and the corresponding distance to the center of the metal-coordinated double bond of norbornadiene is 2.051 ± 0.011 Å. The local symmetry of the manganese and the cyclopentadienyl ring is C_{5v}, which implies no localized metal–ring interactions. It has also been observed, in agreement with a number of other structure determinations, that the metal-coordinated olefinic bond is longer than the uncoordinated bond.

Introduction

Fischer and Herberhold[2] have recently prepared a number of interesting organometallic manganese complexes, among them $(C_5H_5)Mn(C_7H_8)(CO)_2$. When $C_5H_5Mn(CO)_3$ was allowed to react with bicyclo[2.2.1]-hepta-2,5-diene (norbornadiene) in the presence of ultraviolet radiation, a yellow-brown solid was obtained. This was identified as the monosubstitution product $(C_5H_5)Mn(C_7H_8)(CO)_2$. On the basis of infrared (ir) and proton magnetic resonance (pmr) studies in solution, the manganese atom was postulated to be bonded to norbornadiene in an *exo* configuration so that only one of the double bonds was coordinated to the metal. In addition, it was proposed that the bridge carbon atom would be situated fairly close to the manganese atom.

This crystal structure determination was undertaken for three reasons: first, to determine if the proposed molecular structure was correct; second, to determine if there were any localized interactions[3] between manganese and the cyclopentadienyl ring; and, third, to see if there was any increase in the length of the metal-coordinated double bond of norbornadiene, as has been noted in a number of complexes in which a metal is bonded to a nonconjugated diene.[4–6]

Experimental Section

A rectangular parallelepiped-shaped crystal of dimensions 0.09 × 0.18 × 0.23 mm was selected[7] and mounted in a glass capillary. The oscillation, Weissenberg, and precession photographs indicated 2/m symmetry. The lattice constants and their estimated standard deviations, as determined from the zero-level precession photographs, are (22°, λ(Cu Kα_1) 1.5405 Å): $a = 6.19 \pm 0.02$ Å, $b = 11.16 \pm 0.02$ Å, $c = 8.98 \pm 0.02$ Å, and $\beta = 98.50 \pm 0.7°$. The only observed systematic extinctions (precession films) were for $0k0$ data for k odd, this indicating the possible space groups $P2_1$ or $P2_1/m$.

The calculated density of 1.61 g/cm^3, for two molecules in the unit cell, agrees quite well with the observed density of 1.57 ± 0.05 g/cm^3 which was determined by means of the flotation method.

A complete set of three-dimensional data using the original crystal mounted along the b axis were taken on a General Electric XRD-5 X-ray unit equipped with a single-crystal orienter, a scintillation counter, and a pulse height analyzer. A total of 1937 reflections was measured out to a 2θ value of 60° using Mo radiation. The linear absorption coefficient[8] for Mo radiation is 12.36 cm^{-1}. An absorption correction was not made. Consideration of the dimensions of the crystal, including the body diagonal, indicates that in all cases the transmission will be greater than 69% and the ratio of the maximum to the minimum transmission factor is only 1.3. The major effect of not including an absorption corection would be that the error in the anisotopic temperature factors would be larger than the implied esd values. The final positional parameters, however, will not have such appreciable errors, and it was felt that neglect of an absorption correction was justified.

The intensities were recorded by means of the balanced-filter peak-height technique[9–11] using a count time of 40 sec and a take-off angle of 8°. The zirconium and yttrium filters were orginally balanced by Wilkes.[11] Approximately 200 reflections were scanned in order to compute a peak-integrated intensity curve.[9]

The intensities of the (400), (040), and (006) reflections were remeasured frequently in order to estimate the extent of crystal decomposition. A decomposition correction was made although

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[1] (a) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contributon No. 2165. (b) Based on part of a thesis submitted by B. Granoff to the Graduate School of Princeton University as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] E. O. Fischer and M. Herberhold, *Experienta, Suppl.*, **9**, 259 (1964).

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

[4] L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 713 (1963).

[5] J. H. van den Hende and W. C. Baird, Jr., *J. Am. Chem. Soc.*, **85**, 1009 (1963).

[6] J. A. Ibers and R. G. Snyder, *Acta Cryst.*, **15**, 923 (1962).

[7] The author wishes to thank R. J. Angelici, Department of Chemistry, Iowa State University, Ames, Iowa, for preparing the compound[2] and making available crystals which were suitable for a single-crystal investigation.

[8] "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1952, Table 3.2.2.B.

[9] L. Alexander and G. Smith, *Acta Cryst.*, **15**, 983 (1962).

[10] R. Young, *Z. Krist.*, **118**, 223 (1963).

[11] C. E. Wilkes, Ph.D. Thesis, Princeton University, 1964.

it was quite small (the total degree of decomposition throughout the entire data-taking period was less than 5%).

The atomic scattering factor for Mn was taken from the Hartree–Fock–Slater tables of Hanson, *et al.*;[12] scattering factors for carbon and oxygen were taken from the tabulation by Ibers[13a] and corrected for anomalous dispersion effects.[13b] All computations were done on an IBM 7074 computer.

Solution of the Structure

The decomposition, peak-integrated intensity, and Lorentz-polarization corrections were applied to each reflection. In addition, σ_{F_o}, the standard deviation of the observed structure factor, was computed. Using the finite difference method, it can be shown that this is given by[14]

$$\sigma_{F_o} = k^{-1/2}[-I_o^{1/2} + (I_o + \sigma_{I_o})^{1/2}] \qquad (1)$$

where k represents a quotient of constants, I_0 is the observed peak intensity, and σ_{I_o}, the standard deviation of the peak intensity, is given by

$$\sigma_{I_o} = [Z + Y + (C_zZ)^2 + (C_yY)^2]^{1/2} \qquad (2)$$

where Z and Y are the peak intensities (counts recorded on the GE scaler × 10) through the zirconium and yttrium filters, respectively, and C_z and C_y are the estimated relative errors in Z and Y, respectively, to account for systematic errors. Both C_z and C_y were assigned values of 0.05 corresponding to a 5% systematic fluctuation in the peak count through the filters. Substitution of eq 2 into eq 1 gives the expression for σ_{F_o} that was employed in this investigation.

All reflections for which $F_o < 2.5\sigma_{F_o}$ were considered unobserved. These reflections, approximately 300 in number, were not included in the least-squares refinement.

On the basis of the Patterson map, it was initially decided to choose the centric space group $P2_1/m$, and the subsequent successful refinement shows that this choice was indeed the correct one. This space group has fourfold general positions[15] so the two molecules in the entire cell must occupy the twofold special set and thus make use of the crystallographic mirror plane. This mirror passes through the manganese, one atom of the cyclopentadienyl group, and the bridge carbon atom of norbornadiene.

The data were sharpened according to the method of Jacobson, *et al.*,[16] and a sharpened three-dimensional Patterson map was computed.[17] An interpretation of the larger peaks yielded the initial x and z coordinates for the manganese atom, the y coordinate being fixed by symmetry. This trial set of coordinates was then used to compute a three-dimensional electron density map.[17] An examination of this map disclosed the positions of the carbonyl group and the cyclopentadienyl ring. These, together with the manganese atom, were then used to compute a second electron density map, and a careful study enabled the norbornadiene moiety to be located.

Four cycles of full-matrix least-squares refinement[17] on the positional parameters of all the atoms resulted in an agreement factor, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, of 24.3%. The function that was minimized in the process of least-squares refinement was $R' = \Sigma w(|F_o| - |F_c|)^2$, where w, the weighting factor for a reflection, is related to the standard deviation by $w = 1/(\sigma_{F_o})^2$. Further refinement would not result in a lowering of the agreement factor. A careful examination of the data revealed the following. All calculated structure factors were much greater than the observed structure factors for the (h03) data (h = 0–6). This was probably due to an improper setting of one of the angles on the single-crystal orienter, resulting in observed intensities which were much too small. These reflections were removed, and, after two cycles of isotropic refinement on the manganese atom and an additional two cycles of refinement on all the atoms, R dropped to 15.6%. Two cycles of anisotropic refinement on manganese, holding the temperature factors of all of the other atoms fixed, were then followed by three cycles of anisotropic refinement on all of the atoms. A careful check revealed that there was no extinction problem. Although there was a significant drop in the R factor upon refining anisotropically, it must be remembered that, owing to the lack of an absorption correction, the anisotropic thermal parameters are probably suspect. For 1550 observed reflections the final agreement factor was 9.1%. In the final cycle of refinement, the parameter shifts were insignificant with respect to the estimated standard deviations. Standard deviations were calculated assuming relative rather than absolute weights.

A difference electron density map was computed[17] at this point, but it contained no peaks of height greater than 0.8 e$^-$/Å^3. An attempt was made to locate the hydrogen atoms, but this was not completely successful and therefore was abandoned.

A listing of the observed and absolute values of the calculated structure factors (×10) is given in Table I. The final positional and anisotropic thermal parameters as obtained from the final least-squares cycle are given in Tables II and III. Intramolecular distances and bond angles together with estimated standard deviations are tabulated in Table IV. The Busing–Martin–Levy function and error program ORFFE[18] was used for the distance and angle calculations in which the errors were obtained from the full variance–covariance matrix.

Discussion of the Structure

The molecular structure of $(C_5H_5)Mn(C_7H_8)(CO)_2$ is shown in Figure 1. The model originally proposed by Fischer and Herberhold[2] has been shown to be correct. The bridge carbon atom (C_4) is closer to the manganese atom than is any of the other nonbonded carbon atoms

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[12] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, **17**, 1040 (1964).

[13] (a) J. A. Ibers, ref 8, Table 3.3.1; (b) J. A. Ibers, ref 8, Table 3.3.2 C.

[14] (a) B. Granoff, Thesis, Princeton University, 1966; (b) D. E. Williams and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 1660 (1964).

[15] See ref 8, Vol. I.

[16] R. A. Jacobson, J. A. Wunderlich, and W. N. Lipscomb, *Acta Cryst.*, **14**, 598 (1961).

[17] D. R. Fitzwater and J. E. Benson, and J. J. Jackobs, Least-Squares Package, private communication, 1965.

[18] W. R. Busing, K. O. Martin, and H. A. Levy, ORFFE, A Fortran Crystallographic Function and Error Program, Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS (×10) FOR $(C_5H_5)Mn(C_7H_8)(CO)_2$

H	K	FO	FC
L= 0**			
1	0	500	636
2	0	107	142
4	0	254	290
5	0	117	136
7	0	83	81
8	0	22	23
1	1	385	412
2	1	99	93
4	1	145	155
5	1	136	133
7	1	28	37
8	1	70	69
1	2	471	681
2	2	173	139
3	2	262	255
5	2	122	120
6	2	56	58
7	2	77	75
1	3	89	62
2	3	472	464
4	3	118	118
5	3	124	133
6	3	55	61
8	3	39	41
0	4	134	147
1	4	162	139
3	4	253	267
4	4	191	195
6	4	78	79
7	4	54	56
8	4	14	28
1	5	292	275
2	5	219	214
3	5	216	232
4	5	96	117
5	5	144	153
6	5	38	44
8	5	24	30
0	6	140	126
2	6	16	16
3	6	187	201
4	6	157	160
5	6	15	36
6	6	53	66
7	6	46	55
1	7	189	187
2	7	271	276
3	7	87	90
4	7	31	43
5	7	57	108
6	7	70	79
0	8	125	122
1	8	155	166
2	8	60	51
3	8	139	131
4	8	61	67
5	8	30	29
6	8	57	61
7	8	39	48
1	9	180	177
2	9	160	161
3	9	56	52
5	9	86	87
6	9	49	55
0	10	217	204
1	10	83	78
2	10	12	16
3	10	63	66
4	10	13	18
6	10	29	36
1	11	100	95
2	11	88	91
3	11	50	54
4	11	39	49
5	11	58	55
0	12	70	75
1	12	68	71
3	12	76	81
4	12	38	44
1	13	44	29
2	13	81	82
3	13	33	13
4	13	58	40
0	14	56	47
1	14	54	42
2	14	42	14
3	14	64	54
1	15	40	39
2	15	47	33
L= 1**			
0	0	454	627
1	0	213	206
2	0	463	390
3	0	244	213
4	0	283	252
5	0	34	63
6	0	87	71
7	0	117	104
8	0	70	54
0	1	326	372
1	1	481	575
2	1	185	177
3	1	135	117
4	1	116	113
5	1	107	80
6	1	123	98
7	1	32	10
8	1	54	37
0	2	241	280
1	2	156	165
2	2	107	93
3	2	339	318
4	2	200	181
5	2	66	51
6	2	74	57
7	2	111	91
8	2	52	39
0	3	123	131
1	3	104	92
2	3	237	225
3	3	140	138
4	3	91	85
5	3	152	134
6	3	116	98
7	3	33	5
8	3	44	27
0	4	262	246
1	4	317	289
2	4	206	183
3	4	128	116
4	4	220	198
5	4	40	34
6	4	48	61
7	4	36	45
8	4	35	25
0	5	199	167
1	5	149	135
2	5	117	115
4	5	107	106
5	5	230	207
6	5	77	67
7	5	39	7
8	5	41	23
0	6	286	253
1	6	311	289
2	6	85	64
3	6	77	72
4	6	174	160
5	6	51	32
6	6	45	34
7	6	52	35
0	7	54	35
1	7	92	85
2	7	253	249
3	7	94	82
4	7	117	105
5	7	123	108
6	7	90	77
7	7	34	12
0	8	214	182
1	8	230	204
2	8	50	27
3	8	162	144
4	8	79	65
5	8	66	49
6	8	37	9
7	8	64	45
0	9	77	57
1	9	162	144
2	9	235	209
3	9	68	51
4	9	53	31
5	9	74	60
6	9	81	60
0	10	187	162
1	10	155	145
2	10	56	29
3	10	79	61
4	10	85	72
5	10	47	32
0	11	43	45
1	11	94	94
2	11	100	103
3	11	59	61
5	11	48	50
6	11	27	29
0	12	73	74
1	12	59	67
2	12	15	25
3	12	53	54
4	12	57	59
2	13	59	63
3	13	46	45
4	13	18	17
0	14	44	48
1	14	36	38
3	14	24	38
0	15	17	23
2	15	26	33
-2	1	157	180
-3	1	90	83
-4	1	212	220
-5	1	243	205
-7	1	45	52
-8	1	65	65
-1	2	452	499
-2	2	289	274
-3	2	254	260
-4	2	113	112
-5	2	15	9
-6	2	84	94
-7	2	38	48
-1	3	405	434
-2	3	267	268
-3	3	241	202
-4	3	173	174
-5	3	178	183
-6	3	33	36
-1	4	72	102
-2	4	262	267
-3	4	387	404
-4	4	165	178
-5	4	30	28
-6	4	46	57
-7	4	53	56
-1	5	70	83
-2	5	165	168
-3	5	36	38
-4	5	230	230
-5	5	82	84
-6	5	11	22
-8	5	54	50
-1	6	95	84
-2	6	176	173
-3	6	302	304
-4	6	137	143
-6	6	60	69
-7	6	63	67
-1	7	156	164
-3	7	20	14
-4	7	48	41
-5	7	86	94
-7	7	33	35
-1	8	33	25
-2	8	187	183
-3	8	90	85
-4	8	14	100
-6	8	97	93
-7	8	44	50
-1	9	150	146
-2	9	84	77
-3	9	50	45
-4	9	13	25
-5	9	80	85
-6	9	14	21
-7	9	17	26
-2	10	31	34
-3	10	81	87
-4	10	57	61
-5	10	25	29
-6	10	59	57
-1	11	80	77
-2	11	84	81
-3	11	24	21
-4	11	61	65
-5	11	45	48
-1	12	51	52
-2	12	39	44
-3	12	84	87
-4	12	18	27
-1	13	66	67
-2	13	74	74
-4	13	38	50
-1	14	24	33
-2	14	22	35
-3	14	52	56
-1	15	43	48
-2	15	30	37
L= 2**			
0	0	179	142
1	0	519	567
2	0	61	76
3	0	11	9
4	0	73	83
5	0	100	103
6	0	30	29
7	0	59	62
8	0	31	33
0	1	144	126
1	1	278	306
2	1	594	625
3	1	352	347
4	1	32	14
5	1	134	132
6	1	118	128
7	1	63	66
0	2	345	408
1	2	120	133
2	2	187	198
3	2	74	77
4	2	160	168
5	2	73	70
6	2	20	20
7	2	63	62
8	2	19	31
0	3	50	52
1	3	19	11
2	3	197	235
3	3	338	360
4	3	17	6
5	3	111	110
6	3	95	92
7	3	21	31
0	4	261	305
1	4	202	242
2	4	116	146
3	4	65	85
4	4	190	205
5	4	90	89
6	4	25	36
7	4	38	48
0	5	280	331
1	5	39	29
2	5	161	179
3	5	118	113
4	5	48	48
5	5	104	106
6	5	69	68
0	6	222	226
1	6	302	342
2	6	66	68
3	6	83	100
4	6	153	161
5	6	76	78
7	6	32	38
0	7	148	142
1	7	68	82
2	7	144	156
3	7	83	82
4	7	36	32
5	7	54	57
6	7	51	57
7	7	18	20
0	8	237	236
1	8	211	217
2	8	85	83
3	8	128	127
4	8	98	98
5	8	46	52
6	8	14	21
7	8	30	38
0	9	99	96
1	9	96	97
2	9	160	161
3	9	43	46
4	9	22	21
5	9	31	33
6	9	48	53
0	10	109	106
1	10	181	186
3	10	63	64
4	10	63	67
5	10	56	56
0	11	54	59
1	11	49	52
2	11	91	94
3	11	50	55
4	11	18	17
5	11	23	30
0	12	73	74
1	12	58	61
2	12	26	35
3	12	19	23
4	12	65	64
5	12	31	32
0	13	11	17
2	13	29	39
3	13	69	65
0	14	44	45
1	14	39	34
0	15	30	34
-2	1	305	305
-3	1	22	24
-4	1	229	225
-5	1	131	127
-7	1	63	64
-8	1	40	45
-1	2	46	3
-2	2	362	368
-3	2	149	145
-4	2	111	113
-5	2	96	103
-6	2	113	129
-7	2	30	39
-1	3	534	537
-2	3	255	230
-3	3	27	45
-4	3	181	177
-5	3	134	134
-7	3	27	36
-8	3	53	52
-1	4	120	128
-2	4	244	248
-3	4	277	278
-4	4	28	21
-5	4	76	76
-6	4	55	62
-7	4	50	53
-1	5	265	291
-2	5	304	308
-3	5	98	102
-4	5	192	182
-5	5	39	39
-6	5	14	26
-7	5	41	44
-8	5	46	53
-1	6	64	68
-2	6	156	161
-3	6	242	240
-4	6	23	27
-6	6	57	64
-7	6	43	46
-1	7	263	260
-2	7	38	15
-3	7	64	61
-4	7	67	62
-5	7	83	80
-7	7	53	56
-1	8	26	26
-2	8	135	142
-3	8	74	77
-4	8	103	109
-5	8	30	35
-6	8	76	76
-7	8	19	28
-1	9	104	102
-2	9	20	23
-4	9	68	76
-5	9	67	69
-7	9	36	45
-1	10	21	20
-2	10	57	59
-3	10	106	112
-4	10	33	38
-6	10	50	54
-1	11	54	63
-2	11	51	53
-3	11	34	43
-4	11	65	65
-5	11	31	42
-2	12	72	81
-3	12	70	72
-1	13	95	94
-2	13	49	47
-4	13	46	47
-2	14	43	48
-3	14	49	50
-1	15	45	48
-2	15	32	39
L= 3**			
7	0	10	16
0	1	329	337
1	1	42	52
2	1	328	331
3	1	160	172
4	1	21	16
5	1	79	83
6	1	100	103
7	1	43	49
1	2	294	280
2	2	337	333
3	2	19	11
4	2	175	170
5	2	18	62
7	2	13	24
0	3	222	239
1	3	180	175
2	3	136	140
3	3	256	260
4	3	78	75
5	3	84	85
6	3	90	93
7	3	38	42
0	4	245	216
1	4	290	292
2	4	222	214
3	4	47	56
4	4	95	88
5	4	82	86
6	4	13	5
7	4	45	43
0	5	172	160
1	5	31	19
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-6	5	26	30
-3	6	40	44
-4	6	57	49
-5	6	47	10
-2	7	45	49
-3	7	26	22
-5	7	29	37
-1	8	56	53
-3	8	62	53
-4	8	44	44
-1	9	22	22
-2	9	37	42
-1	10	26	33
-3	10	37	39
L= 10**			
0	0	59	61
3	0	16	18
4	0	39	42
0	1	17	0
1	1	54	51
2	1	41	45
0	2	33	56
1	2	11	15
3	2	37	28
4	2	33	35
0	3	13	12
1	3	54	51
2	3	60	55
0	4	43	47
1	4	37	40
3	4	33	42
1	5	45	44
2	5	46	50
0	6	34	42
1	6	27	38
3	6	41	45
1	7	12	22
0	8	41	40
1	8	17	20
-1	1	78	73
-2	1	106	96
-3	1	34	36
0	2	54	56
-1	2	54	51
-2	2	32	27
-3	2	55	49
-6	2	31	34
-1	3	36	40
-2	3	47	48
-3	3	21	29
-5	3	36	40
-1	4	12	29
-3	4	31	35
-4	5	21	30
-5	5	34	37
-1	6	27	20
-3	6	25	34
-1	7	30	41
-2	7	20	36
-1	8	25	25
-3	8	22	25
-1	9	44	45
-2	9	35	40

of the norbornadiene moiety. Although the hydrogen atoms were not located, it is easy to see that one of them, which is bonded to C_4, is probably also quite close to the manganese atom. This would account for the large high-field shift in the pmr spectrum (τ 6.72) Similar shifts have been observed for a number of transition metal hydrides.[19,20]

A listing of some of the important distances and angles found in $(C_5H_5)Mn(C_7H_8)(CO)_2$ and the corresponding values found in $(C_5H_5)Mn(CO)_3$[21] is given in Table V. In particular, the average Mn–C_5H_5 distance of 2.168 Å in the norbornadiene complex compares favorably with the corresponding distance of 2.151 Å found in $(C_5H_5)Mn(CO)_3$. The average ring C–C distances in the two compounds also agree quite well.

The Mn–CO distance of 1.794 ± 0.007 Å compares well with the corresponding average distances obtained

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TABLE II

FINAL POSITIONAL PARAMETERS, WITH STANDARD DEVIATIONS, FOR $(C_5H_5)Mn(C_7H_8)(CO)_2$ IN FRACTIONS OF THE UNIT CELL EDGES

Atom	x	y	z
Mn	0.3531 (2)[a]	0.2500[b]	0.0508 (1)
C_2	0.6084 (8)	0.3126 (5)	0.2250 (6)
C_1	0.5848 (12)	0.3520 (6)	0.3836 (7)
C_3	0.8036 (14)	0.3114 (8)	0.4757 (9)
C_4	0.4309 (19)	0.2500[b]	0.4283 (11)
C_5	0.5825 (17)	0.2500[b]	−0.1112 (11)
C_6	0.4534 (16)	0.3503 (6)	−0.1338 (7)
C_7	0.2368 (14)	0.3131 (6)	−0.1740 (7)
C_8	0.2048 (9)	0.3650 (4)	0.1298 (7)
O_1	0.1102 (8)	0.4417 (4)	0.1773 (6)

[a] Numbers in parentheses here and in succeeding tables are the estimated standard deviations in the least significant digits. [b] These coordinates are fixed by symmetry.

TABLE III

FINAL ANISOTROPIC THERMAL COEFFICIENTS[a] ($\times 10^4$) FOR $(C_5H_5)Mn(C_7H_8)(CO)_2$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	189 (3)	56 (1)	114 (1)	0[b]	18 (1)	0[b]
C_2	229 (14)	110 (4)	148 (8)	−14 (7)	−4 (9)	−14 (5)
C_1	394 (23)	181 (8)	140 (9)	−22 (11)	−8 (1)	−29 (7)
C_3	510 (30)	275 (14)	176 (12)	−8 (2)	−64 (16)	−36 (9)
C_4	500 (41)	254 (17)	158 (15)	0[b]	114 (21)	0[b]
C_5	326 (30)	301 (21)	129 (13)	0[b]	78 (16)	0[b]
C_6	751 (41)	118 (7)	142 (10)	−126 (13)	67 (16)	16 (6)
C_7	603 (31)	142 (7)	144 (9)	116 (12)	−6 (1)	23 (6)
C_8	271 (16)	72 (4)	179 (9)	−2 (1)	24 (10)	−10 (5)
O_1	441 (17)	99 (4)	300 (10)	54 (7)	132 (10)	−25 (5)

[a] These are of the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. [b] These thermal parameters are fixed at zero by symmetry.

TABLE IV

INTRAMOLECULAR DISTANCES AND ANGLES FOR $(C_5H_5)Mn(C_7H_8)(CO)_2$

Atoms	Distance, Å	Atoms	Angle, deg
$Mn{-}C_2$	2.169 (6)	$O_1{-}C_8{-}Mn$	177.8 (7)
$Mn{-}C_1$	3.354 (12)	$C_8{-}Mn{-}C_8'$	91.9 (4)
$Mn{-}C_3$	4.435 (9)	$C_2{-}C_2{-}C_3$	102.7 (8)
$Mn{-}C_4$	3.321 (8)	$C_2{-}C_2'{-}C_1'$	104.1 (8)
$Mn{-}C_5$	2.178 (12)	$C_1{-}C_3{-}C_3'$	105.0 (1.0)
$Mn{-}C_6$	2.166 (8)	$C_2{-}C_1{-}C_4$	100.1 (7)
$Mn{-}C_7$	2.159 (8)	$C_1{-}C_4{-}C_1'$	92.6 (10)
$Mn{-}Cl$	1.794 (7)	$C_4{-}C_1{-}C_3$	100.6 (9)
Mn–A	2.051 (11)[a]	$C_5{-}C_6{-}C_7$	108.1 (8)
Mn–B	1.805 (9)[b]	$C_6{-}C_7{-}C_7'$	107.3 (5)
$C_2{-}C_2'$	1.397 (13)	$C_6{-}C_5{-}C_6'$	109.3 (1.2)
$C_1{-}C_2$	1.519 (10)	$A{-}Mn{-}C_8$	122.6 (9)
$C_1{-}C_2$	1.547 (13)	$B{-}Mn{-}C_8$	94.6 (9)
$C_3{-}C_3'$	1.360 (22)	A–Mn–B	120.3 (1.1)
$C_1{-}C_4$	1.574 (13)		
$C_2{-}C_3$	2.407 (17)		
$C_1{-}C_1'$	2.277 (18)		
$C_5{-}C_6$	1.383 (12)		
$C_6{-}C_7$	1.400 (14)		
$C_7{-}C_7'$	1.407 (17)		
$C_8{-}O_1$	1.154 (8)		

[a] A is the midpoint of $C_2{-}C_2'$. [b] B is the center of the cyclopentadienyl ring.

by X-ray diffraction in $Mn_2(CO)_{10}$ (1.82 Å),[22] $HMn(CO)_5$ (1.83 Å),[23] and $(C_5H_5)Mn(CO)_3$ (1.80 Å).[21] The C–O distance of 1.154 ± 0.008 Å also compares favorably with the corresponding average distances (1.13–1.17 Å) found in a number of other molecules.[22–26]

The observed Mn–C–O bond angle of 177.8 ± 0.7° differs significantly from 180°, as has also been observed in other carbonyl complexes.[22–26] It can be seen that, in most cases, there is a considerable deviation from the expected linearity. It is generally accepted that the bonding in transition metal carbonyls consists of: (i) a forward donation of electrons from a nonbonding σ-type orbital localized on the carbon atom to an empty metal orbital of the appropriate symmetry and (ii) a back-donation of charge from a filled d orbital to an

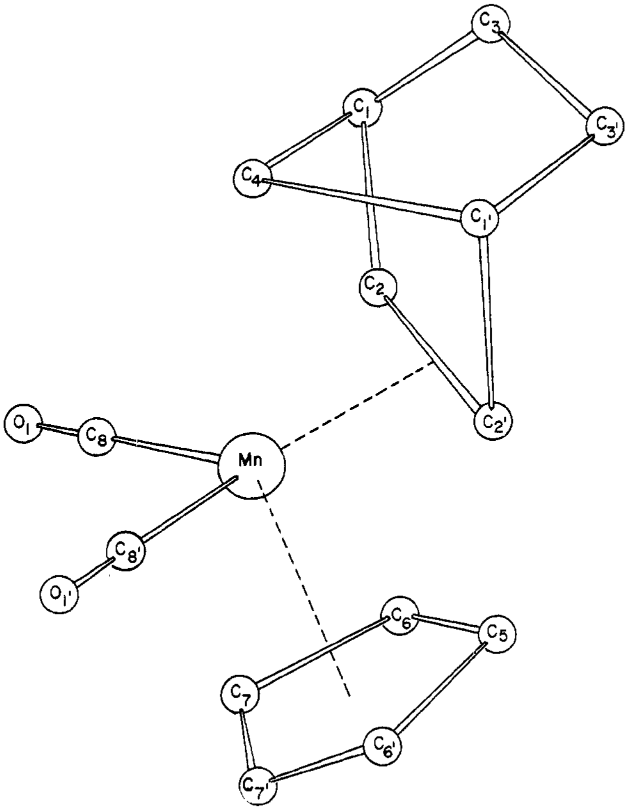

Figure 1.—The molecular configuration of $(C_5H_5)Mn(C_7H_8)(CO)_2$.

TABLE V

COMPARISON OF SELECTED AVERAGE BOND DISTANCES AND ANGLES[a] IN $(C_5H_5)Mn(C_7H_8)(CO)_2$ AND $(C_5H_5)Mn(CO)_3$[a]

Quantity	$(C_5H_5)Mn(C_7H_8)(CO)_2$	$(C_5H_5)Mn(CO)_3$[b]
$Mn{-}C_{carbonyl}$	1.794 (7)[c]	1.797 (20)[c]
$Mn{-}C_{ring}$	2.168 (9)	2.151 (25)
C–O	1.154 (8)	1.134 (30)
$C_{ring}{-}C_{ring}$	1.397 (14)	1.394 (30)
Mn–C–O	177.7 (7)	178.0
OC–Mn–CO	91.9 (4)	92.0
Ring planarity[d]	0.004	0.02

[a] Bond distances are in ångströms and bond angles are in degrees. See ref 21. [b] Estimated standard deviations for the bond angles were not given. [c] Deviation is average estimated standard deviation. [d] Maximum derivation from least-squares plane.

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empty π^*-antibonding orbital of the carbonyl group.[27,28] It is important to realize as has been pointed out by Kettle for complexes containing the metal $(CO)_3$ group[29,30] that the two π^*-antibonding orbitals of each carbonyl group will have different symmetry properties. Each of the π^* orbitals of a carbonyl group is perpendicular to the metal–C–O axis, but whereas one of these orbitals is symmetric to reflection, the other orbital is antisymmetric. In more general cases it can be shown that each of the two sets of π^* orbitals on a carbonyl group will transform according to a different irreducible representation.

Therefore, there is no *a priori* reason to expect the metal orbitals to interact equally with the two different π^* orbitals. Because of these unequal interactions, cylindrical symmetry about the metal–C–O axis should not be observed, and the deviations which are actually found can be rationalized in terms of these simple MO considerations.

The cyclopentadienyl C–C bond lengths in $(C_5H_5)Mn(C_7H_8)(CO)_2$ are all equal within 2 estimated standard deviations. The average C–C ring distance of 1.397 Å compares favorably with the corresponding average distances (1.39–1.43 Å) found in a number of other structures.[31–36] All of the bond angles are within 1.2° of 108°, which is the angle of the regular pentagon. The observed equality of the $Mn–C_5H_5$ distances, the ring C–C bond distances and bond angles, and the fact that the ring is planar to within 0.004 Å demonstrate the C_{5v}-localized symmetry of the $Mn–C_5H_5$ portion of the molecule. In a number of cases, the concept of localized bonding[3,4] has been invoked to explain the observed variations in the cyclopentadienyl bond lengths and in the metal–C_5H_5 bond lengths.[37–39] It has recently been shown by Abrahams and Ginsberg,[40] however, that in some of these structures the X-ray data are of such poor quality that the reported C–C bond length variations are *not* statistically significant. It must be concluded, therefore, on the basis of the present X-ray data, that there is no evidence for any localized metal–ring interactions in $(C_5H_5)Mn(C_7H_8)(CO)_2$.

It is informative to compare some of the bond distances and angles of the norbornadienyl group in $(C_5H_5)Mn(C_7H_8)(CO)_2$ with the corresponding values found in $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$,[4] $C_7H_8PdCl_2$,[41] $(C_7H_8CuCl)_4$,[42] and the norbornadiene molecule itself.[43] The parameters for norbornadiene have recently been obtained by means of gas-phase electron diffraction using sharpened radial distribution curves. The necessary data are listed in Table VI.

Table VI

Comparison of Norbornadienyl Geometry in $(C_5H_5)Mn(C_7H_8)(CO)_2$, $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$,[4] $C_7H_8PdCl_2$,[41] $(C_7H_8CuCl)_4$,[42] and C_7H_8[43]

Atoms	$(C_5H_5)Mn(C_7H_8)(CO)_2$	$C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$	$C_7H_8PdCl_2$	$(C_7H_8CuCl)_4$	C_7H_8
		Intramolecular Distances, Å			
$C_2–C_2'$	1.397 (13)	1.450 (16)	1.366 (10)	1.345 (11)	1.35
$C_3–C_3'$	1.360 (22)	1.330 (21)	1.366 (10)	1.317 (11)	1.35
$C_1–C_3$	1.547 (13)	1.529 (19)	1.552 (6)	1.517 (11)	
$C_1–C_2$	1.519 (10)	1.551 (19)	1.554 (6)	1.549 (11)	1.55[a]
$C_1–C_4$	1.574 (13)	1.522 (20)	1.547 (6)	1.534 (11)	
$C_1–C_1'$	2.277 (18)	2.26	2.25[b]	2.226 (11)	2.29
$C_2–C_3$	2.407 (17)	2.50	2.38[b]	2.386 (11)	2.37
		Bond Angles, Deg			
$C_2–C_1–C_3$	102.7 (8)	108.6 (1.2)	100.3 (3)	104.1 (4)	104
$C_2–C_2–C_1$	104.1 (8)	105.6 (1.0)	106.9 (4)	105.9 (3)	108
$C_1–C_3–C_3'$	105.0 (1.0)	104.7 (1.4)	107.0 (4)	105.9 (3)	108
$C_2–C_1–C_4$	100.1 (7)	92.6 (1.1)	99.5 (4)	97.6 (4)	98
$C_3–C_1–C_4$	100.6 (9)	103.7 (1.0)	100.4 (4)	100.9 (5)	97
$C_1–C_4–C_1'$	92.6 (10)	94.8 (1.1)	93.8[b]	97.5 (4)	97

[a] Only the average C–C distance was reported. [b] Computed from reported data.

It is apparent that the basic geometry of the norbornadienyl moiety is essentially the same in the complexed state as it is in the free molecule. The $Mn–C_7H_8$ distance of 2.169 Å is in agreement with the corresponding mean copper–olefin distance of 2.081 Å found in $(C_7H_8CuCl)_4$. The distance from the manganese to the midpoint of $C_2–C_2'$ is 2.051 Å and compares favorably with the corresponding value of 1.971 Å in $(C_7H_8CuCl)_4$.[42]

The bicyclic ring system remains highly strained in the complexed state. This is seen in the bridge angle ($C_1–C_4–C_1'$) of 97° found in norbornadiene itself and in the similar angles observed in the complexes (Table VI). It is interesting to note that even in the nickel complex, where the bridge carbon (C_4) is involved in the bonding to the metal, the ring strain is still pronounced in the 94.8° bridge angle and in the $Ni–C_4–C_1$ and $Ni–C_4–C_1$, bond angles of 93.2 and 92.8°, respectively.[4]

The only noticeable change in the geometry of the norbornadienyl moiety, in some of the complexes, is the increased length of the metal-coordinated olefin bond, *i.e.*, $C_2–C_2'$. In most cases this increase in bond length is on the borderline of statistical significance, but the ir spectra usually show a decrease of about 100 cm^{-1} in the C=C stretch in going from the free to the metal-coordinated olefin,[44] and such an effect was found in the study of this compound.[2] On the basis of both the ir and the present X-ray study it appears as if the double

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bond (C_2–C_2') that is coordinated to manganese is significantly longer than the uncoordinated bond. This increase in the length of a double bond upon coordination with a metal is most likely due to a decrease in the π-bond order.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS 60201

The Structure of Tris(ethylenediamine)chromium(III) Hexacyanocobaltate(III) Hexahydrate, $[Cr(C_2H_8N_2)_3]$ $[Co(CN)_6]\cdot 6H_2O$

BY KENNETH N. RAYMOND AND JAMES A. IBERS

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The structure of tris(ethylenediamine)chromium(III) hexacyanocobaltate(III) hexahydrate, $[Cr(C_2H_8N_2)_3][Co(CN)_6]\cdot 6H_2O$, has been determined from three-dimensional X-ray data collected by counter methods. The final R factor on F for the 1035 F^2 values above $\sigma(F^2)$ is 9.4%, and for the 735 reflections above $3\sigma(F^2)$ it is 6.1%. The material crystallizes with four molecules in space group C_{2h}^6-I2/a of the monoclinic system in a cell of dimensions $a = 16.745$ (20), $b = 10.546$ (15), $c = 14.331$ (20) Å, $\beta = 96.9$ (1)°. The measured and calculated densities are both 1.46 g/cm^3. The site symmetry at Co is $\bar{1}$; that at Cr is 2. The structure consists of discrete $Cr(C_2H_8N_2)_3^{3+}$ cations and $Co(CN)_6^{3-}$ anions. Hydrogen bonding connects the anions, cations, and water molecules. The $Cr(C_2H_8N_2)_3^{3+}$ cation has its expected coordination geometry. For a Λ configuration of the cation the conformation of the complex is $\Lambda\lambda\lambda\lambda$. The average Cr–N, N–C, and C–C distances are 2.081 (5), 1.481 (12), and 1.489 (9) Å. The $Co(CN)_6^{3-}$ anion has its expected octahedral geometry. The average Co–C distance is 1.869 Å, although the three independent Co–C distances appear to differ slightly. The average C–N distance is 1.155 (8) Å.

Introduction

The successful isolation of the pentacyanonickelate(II) ion[1] prompted attempts[2] to isolate the $HCo(CN)_5^{3-}$ ion and the $Co(CN)_5^{3-}$ ion by precipitation with a large counterion of charge +3. The decomposition of $Co(CN)_5^{3-}$ ion in aqueous solutions is apparently catalyzed by $Cr(en)_3^{3+}$ (en = $NH_2CH_2CH_2NH_2$ = $C_2H_8N_2$).[3] Attention was therefore focused on the $HCo(CN)_5^{3-}$ ion.[4] Yellow crystals of what was believed to be the $Cr(en)_3^{3+}$ salt of $HCo(CN)_5^{3-}$ were isolated. Chemical analysis of this compound did not definitely distinguish among the $Co(CN)_5(OH)^{3-}$, $HCo(CN)_5^{3-}$, and $Co(CN)_6^{3-}$ salts, particularly since the exact number of waters of hydration was uncertain to within $\pm {}^1/_2H_2O$.

An infrared band at 2030 cm^{-1}, which disappeared upon deuteration, was interpreted as a Co–H stretching mode. The $Cr(en)_3^{3+}$ salts of $Co(CN)_5(OH)^{3-}$ and $Co(CN)_6^{3-}$ were prepared by combining their aqueous solutions at room temperature. In both cases the infrared spectra of the resulting compounds were very different from what was believed to be the hydride salt. At this point, in an attempt to supplement the chemical and spectroscopic information at hand, we undertook a rapid X-ray determination of the structure of the compound. This determination proved that the material is $[Cr(en)_3][Co(CN)_6]\cdot 6H_2O$. This salt has subsequently been made by the more direct method of combining aqueous $[Cr(en)_3]Cl_3$ and $K_3[Co(CN)_6]$ solutions. The hexahydrate is obtained only at low temperatures and rapidly effloresces when opened to the air. The infrared spectrum of the compound prepared in this way is identical, including the band at 2030 cm^{-1}, with that of what was initially characterized as the hydride. When the first few waters of hydration are lost, this band disappears, and those bands which correspond to C–N stretching vibrations change markedly.

Even though the material prepared was not the one hoped for, we persisted with the refinement of the structure for the following reasons. First, we found earlier that the conformations of the two independent tris(ethylenediamine)chromium(III) ions in the pentacyanonickelate(II) salt were different[5] from that found previously (and generally believed to be most stable). We postulated that hydrogen bonding specifically favors these different conformers. Since the present hexahydrate salt should exhibit considerable hydrogen bonding, it seemed of interest to determine the conformation of the tris(ethylenediamine)chromium(III) in the present structure. Second, there are no reliable data for any of the hexacyanides[6] and it was therefore

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