these bonds are single in character. In $RhI_2(CH_3)(P(C_6H_5)_3)_2$,[22] which has a tetragonal pyramidal configuration about Rh with CH_3 at the apex, the Rh–CH_3 distance is 2.081 (9) Å. If we take the normal covalent radius of C as 0.77 Å,[30] then a covalent radius of Rh of 1.31 Å may be derived. If one assumes a normal covalent radius of S of 1.04 Å,[30] then one predicts the length of a Rh–S single bond to be 2.35 Å, some 0.1 Å shorter than observed here. However, if one takes the radius of S in the SO_2^- ion to be half the S–S distance in the dithionite ion, namely, 1.20 Å, then one predicts a Rh–SO_2^- distance of 2.51 Å, closer to that observed here.

It would thus appear that the rationalization presented in the Introduction is a useful one in describing the varying geometries exhibited by NO and SO_2 in transition metal complexes. However, it is far from clear why NO and SO_2 may act either as Lewis acids or Lewis bases and why in their attachment to the $MX(CO)(P(C_6H_5)_3)_2$ systems (M = Ir or Rh, X = halogen) they should exhibit a Lewis acid character. This behavior must certainly be contrasted with the bonding of molecular oxygen,[16,17] tetracyanoethylene,[29] *trans*-1,2-dicyanoethylene,[31] and tetrafluoroethylene[32] in these systems, where the π-bonding scheme of Chatt and Dewar seems most applicable. Of even more interest, the contrast between the structures of $IrCl(CO)(NO)(P(C_6H_5)_3)_2^+$ and the formally isoelectronic $IrCl(CO)_2(P(C_6H_5)_3)_2$ molecule[33] is striking. As already indicated, in the NO complex the iridium coordination polyhedron is a tetragonal pyramid, with the apical NO group bonded to iridium through an Ir–N σ bond; in the bis-CO complex a trigonal-bipyramidal configuration is found, with *trans*-phosphine ligands and normal Ir–C–O geometries.

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Nature of the Metal–Hydrogen Bond in Transition Metal–Hydrogen Complexes: Neutron and X-Ray Diffraction Studies[1] of β-Pentacarbonylmanganese Hydride

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An X-ray and neutron diffraction study of a new crystalline form of $HMn(CO)_5$, hereafter designated β-$HMn(CO)_5$, is described. The material crystallizes with eight molecules in space group C_{2h}^6-C2/c of the monoclinic system in a cell (measured at −75°) of dimensions a = 12.16 (3) Å, b = 6.28 (2) Å, c = 19.34 (4) Å, and β = 91.2 (5)°. The structural details involving the nonhydrogen atoms derived from 596 visually estimated independent X-ray intensities collected at −75° and from 398 independent neutron diffraction counter data collected at −105° agree within the assigned limits of error. In addition, a precise position for the hydrogen atom has been derived from the neutron data. The β-$HMn(CO)_5$ molecule deviates only slightly from C_{4v} symmetry. The Mn–C_{ax} bond length is 1.882 (12) Å, while the average Mn–C_{eq} bond length is 1.853 (12) Å (ax = axial, *trans* to H; eq = equatorial, *cis* to H). The equatorial carbonyl groups are bent toward the hydrogen atom; the C_{ax}–Mn–C_{eq} bond angles range from 94.9 (5) to 98.2 (5)°. The Mn–C–O linkages do not deviate significantly from linearity. Thus the molecular structures of α- and β-$HMn(CO)_5$ are essentially identical, but the crystal structures differ markedly and these differences are dicussed. The Mn–H distance in β-$HMn(CO)_5$ is 1.601 (16) Å. This value, the first to be determined with such precision in a parent transition metal carbonyl hydride, is consistent with the usual covalent radii sums and with earlier, less accurate X-ray determinations of metal–hydrogen distances, but it is totally inconsistent with some theoretical studies and the various interpretations of the broad-line nmr spectra obtained from this and related compounds. From the present study it is concluded that the hydrogen atom is a stereochemically active ligand and that the metal–hydrogen distance is that of a normal covalent bond.

Introduction

The nature of the metal–hydrogen bond in transition metal hydride complexes has been of considerable interest for a number of years. A brief history of the structural aspects of the subject up to the end of 1964 is available.[5] As of that time it was clear from crystallographic studies on various stable hydride complexes[6]

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that the hydrogen is a stereochemically active ligand. However, reliable data on the metal–hydrogen bond length were sparse. As of that time only the Rh–H bond length in $RhH(CO)(P(C_6H_5)_3)_3$[7] (1.60 (12) Å by X-ray diffraction) and the Re–H bond length in the ReH_9^{2-} ion[8] (1.61–1.72 Å by neutron diffraction) were known. No diffraction data on the metal–hydrogen bond lengths in the parent carbonyl hydrides were available, although the results of theoretical calculations[9] and a broad-line nmr study[10] on these systems were interpreted as support for an extremely short metal–hydrogen bond, perhaps 1.1–1.5 Å, in keeping with the original notion[11] that the hydrogen atom was "buried" in the metal orbitals and was not a stereochemically active ligand. It is perhaps worthwhile recalling that it was not until after an X-ray study on α-$HMn(CO)_5$ showed unequivocally[6] that the molecule possesses essentially C_{4v} symmetry with H as a stereochemically active ligand that the infrared data on this compound could be interpreted[12] in a manner consistent with this symmetry. The evidence from the X-ray diffraction study of α-$HMn(CO)_5$ and from other studies[13] was strongly in favor of a metal–hydrogen bond of normal length. Yet, as noted then, it still seemed worthwhile to settle the question beyond any doubt through a neutron diffraction study of $HMn(CO)_5$.

That study, described in this present paper, was delayed by a variety of experimental difficulties. In the interim the need for such a study became even more apparent as broad-line nmr studies on polycrystalline samples of parent carbonyl hydrides[14,15] gave values which were exceptionally short (1.28 ± 0.02 Å for Mn–H in $HMn(CO)_5$ and 1.42 ± 0.05 Å for Co–H in $HCo(CO)_4$). These studies used the Van Vleck[16] second-moment expression which assumes that the nuclei are quantized about the direction of the applied magnetic field. This treatment neglects any quadrupole coupling effects at the ^{55}Mn and ^{59}Co nuclei. However, this approximation has been criticized in two recent communications[17,18] in which quadrupolar coupling at the metal nucleus was considered. However, both interpretations place relatively short values of 1.42 and 1.44 Å on the Mn–H distance in $HMn(CO)_5$. These distances are in remarkable agreement with that of 1.425 ± 0.046 Å derived from electron diffraction studies[19a] on gaseous $HMn(CO)_5$.[19b] Unfortunately, both the published electron diffraction determination and the theoretical approximations made in the nmr studies appear to be incorrect, for the present study provides unequivocal evidence that the Mn–H distance in $HMn(CO)_5$ is 1.601 (16) Å. It is, however, interesting to note that a recent theoretical calculation[20] predicts a distance of 1.60 (±0.07) Å.

X-Ray Structure

Manganese pentacarbonyl hydride was prepared and purified as previously described.[21] Samples were sealed in quartz capillaries of nominal 1-mm diameter, sharply tapered to a point at the end to facilitate nucleation. Crystals were grown by slow cooling from the liquid phase in a stream of cold nitrogen gas using a modification of a previously described apparatus.[22]

X-Ray data were collected at −75° using the precession method. On the basis of the observed Laue symmetry 2/m and the systematic absences $h + k \neq 2n$ for (hkl) and $h \neq 2n$, $l \neq 2n$ for $(h0l)$, the structure may be assigned to the space group C_{2h}^6-C2/c or C_s^4-Cc[23] of the monoclinic system. The former (centrosymmetric) space group was assumed. Cell constants were determined from precession photographs and are a = 12.16 (3) Å, b (unique axis) = 6.28 (2) Å, c = 19.34 (4) Å, β = 91.2 (5)° (λ(Mo Kα) = 0.7107 Å). The calculated density for eight molecules in the cell is 1.762 g cm^{-3}.[24] Although the cell constants are very similar to those obtained in our original X-ray study of $HMn(CO)_5$, the symmetry of the cell is different, and it is clear that we are dealing with a second crystalline phase. Previously we had found a = 12.18 (2) Å, b = 6.35 (1) Å, c = 19.20 (3) Å, β = 93.3 (5)°, and space group C_{2h}^6-I2/a. All efforts in this present study to grow crystals of the original modification, hereafter designated α-$HMn(CO)_5$, were unsuccessful. Consequently, it was highly desirable to determine the structure of the new form, β-$HMn(CO)_5$, by X-ray diffraction techniques in preparation for a neutron diffraction study.

A crystal was aligned with the $(1\bar{1}0)$ direction coincident with the goniometer head axis. The reciprocal lattice nets $hk0$, $hk1$, $hk2$, $hk3$, $h\bar{h}l$, and $h, \bar{h} + 2, l$ were recorded photographically using Zr-filtered Mo Kα radiation, and in this way intensities of 741 reflections, of which 596 are independent, were obtained. The X-ray data were all collected from one crystal, but many

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Table I

Observed and Calculated X-Ray Structure Amplitudes in Electrons for β-HMn(CO)$_5$

K	L	FOBS	FCALC
H= 0			
0	4	66	67
0	6	32	35
0	8	33	30
0	12	39	40
0	18	74	82
2	0	217	228
2	1	69	79
2	2	23	13
2	3	46	48
2	4	47	50
2	6	38	36
2	7	60	54
2	8	54	52
2	11	70	70
2	13	65	58
2	14	64	66
2	15	91	88
2	16	46	34
2	17	37	35
2	18	41	35
4	0	65	69
4	3	48	52
4	8	62	60
4	11	33	28
4	14	76	79
6	0	60	62
6	3	24	23
6	4	99	90
6	5	31	28
H= 1			
1	-18	26	21
1	-17	42	40
1	-16	32	31
1	-15	45	46
1	-11	61	60
1	-10	108	105
1	-9	37	33
1	-8	44	48
1	-7	43	36
1	-6	320	317
1	-5	29	29
1	-4	46	44
1	-3	33	35
1	-2	46	48
1	-1	33	33
1	0	54	53
1	1	23	17
1	2	48	49
1	3	42	47
1	4	46	46
1	5	179	176
1	8	15	5
1	9	77	73
1	11	24	27
1	12	75	76
3	-14	66	72
3	-8	30	36
3	-5	53	56
3	-4	12	7
3	1	88	87
3	2	36	36
3	3	57	58
3	4	46	42
3	5	113	109
3	6	29	27
3	8	95	96
3	9	28	25
3	10	21	13
3	11	25	22
3	12	107	98
3	13	41	41
3	14	43	41
5	-10	23	26
5	-2	57	58
5	0	24	25
5	1	21	16
5	2	49	45
5	5	39	37
H= 2			
0	-18	38	39
0	-16	181	174
0	-14	54	54
0	-12	155	155
0	-8	25	24
0	-6	28	28
0	-4	43	49
0	-2	62	61
0	0	58	62
0	2	59	58
2	-17	39	30
2	-16	28	24
2	-14	54	51
2	-12	37	36
2	-11	32	31
2	-9	98	93
2	-8	24	22
2	-7	48	49
2	-6	41	42
2	-5	34	33
2	-4	97	95
2	-1	247	236
2	0	40	43
2	1	46	52
2	2	20	24
2	3	56	50
2	4	47	46
2	5	45	45
2	6	119	120
2	10	120	119
2	11	36	31
2	13	79	71
2	14	40	42
2	17	47	47
4	-11	25	30
4	-10	26	26
4	-9	40	46
4	-8	41	54
4	-2	65	65
4	-1	48	41
4	1	25	24
4	2	30	26
4	3	95	91
4	4	36	35
4	5	27	25
4	6	116	113
4	9	35	32
4	12	31	26
4	13	48	46
4	14	50	49
6	-2	46	50
6	-1	77	75
6	2	64	62
6	3	80	75
H= 3			
1	-16	17	7
1	-15	82	85
1	-14	21	19
1	-13	16	19
1	-12	71	72
1	-11	24	19
1	-10	80	78
1	-9	66	61
1	-8	32	33
1	-7	131	129
1	-2	55	56
1	0	45	47
1	1	38	36
1	2	65	68
1	3	79	78
1	4	267	275
1	6	19	17
1	7	59	59
1	8	51	57
1	10	29	28
1	12	55	53
1	14	55	56
3	-15	59	60
3	-13	62	62
3	-10	97	105
3	-9	32	34
3	-7	129	123
3	-5	13	15
3	-4	77	80
3	-2	37	38
3	-1	29	25
3	0	97	97
3	2	32	34
3	3	18	17
3	4	47	51
3	5	27	24
3	7	26	27
3	8	61	66
3	13	35	34
3	14	39	35
5	-3	51	55
5	-1	68	65
5	0	111	109
5	3	24	22
H= 4			
0	-18	70	81
0	-16	60	57
0	-14	88	86
0	-10	34	31
0	-8	43	46
0	-6	53	52
0	-2	371	360
0	0	49	48
0	2	96	99
0	4	113	119
2	-13	45	44
2	-12	27	29
2	-9	23	23
2	-8	41	43
2	-7	38	40
2	-6	35	40
2	-5	31	29
2	-3	60	59
2	-2	93	94
2	-1	42	46
2	0	37	37
2	1	46	47
2	2	79	81
2	3	50	50
2	5	67	67
2	6	22	20
2	7	67	72
2	9	38	31
2	10	54	49
2	11	25	28
2	13	38	39
2	14	36	29
2	16	106	109
4	2	45	52
4	3	39	38
4	4	63	57
4	5	17	18
4	6	9	1
4	7	8	19
4	8	20	25
4	9	17	14
4	10	28	24
4	11	16	21
4	12	73	79
4	13	45	46
H= 5			
1	-16	36	37
1	-14	34	35
1	-12	80	76
1	-10	49	46
1	-9	19	17
1	-8	136	135
1	-5	69	66
1	-3	25	21
1	-1	88	93
1	0	38	33
H= 6			
0	-16	52	52
0	-8	101	93
0	-6	47	45
0	-4	105	105
0	0	91	95
0	2	99	92
0	4	84	78
0	6	90	89
2	-15	27	38
2	-11	116	109
2	-10	38	36
2	-9	55	52
2	-8	44	45
2	-7	59	54
2	-6	95	94
2	-5	39	39
2	-3	133	129
2	-1	21	26
2	0	27	25
2	1	62	61
2	2	45	50
2	3	101	97
2	4	60	60
2	5	91	85
2	6	18	6
2	7	36	33
2	8	51	54
2	11	81	76
2	12	51	46
2	13	38	34
2	15	42	44
4	-7	16	22
4	0	60	73
4	1	58	65
4	4	143	140
4	5	36	35
4	6	59	57
4	8	83	79
4	10	26	22
4	11	46	40
H= 7			
1	-15	27	37
1	-14	60	65
1	-13	30	27
1	-12	72	73
1	-10	68	75
1	-9	62	58
1	-7	43	40
1	-6	21	22
1	-5	51	50
1	-3	50	51
1	-1	83	79
1	0	33	30
1	2	92	89
1	3	29	28
1	4	70	70
1	6	40	38
1	7	38	37
1	8	51	54
1	10	55	58
1	11	43	46
1	12	53	53
1	13	44	46
1	15	20	25
3	-1	39	45
3	1	19	18
3	2	32	32
3	5	31	29
3	6	89	97
3	7	60	71
3	8	44	48
3	10	40	47
5	-3	24	32
H= 8			
0	-12	66	68
0	-10	33	31
0	-6	49	50
0	-4	46	47
0	-2	42	41
0	0	51	51
0	2	56	56
0	4	52	46
2	-12	27	28
2	-11	60	63
2	-8	44	37
2	-7	48	46
2	-5	37	36
2	-2	27	19
2	0	78	70
2	1	34	38
2	3	40	42
2	5	56	56
2	7	23	18
2	9	50	47
2	10	30	28
4	-8	29	35
4	-5	30	26
4	-4	45	44
4	-3	55	53
4	-2	40	39
4	-1	38	36
4	0	96	94
4	1	48	46
4	2	114	107
4	3	18	18
4	4	113	103
4	5	33	27
4	6	70	64
H= 9			
1	-12	29	30
1	-11	62	60
1	-10	37	33
1	-6	32	29
1	-5	41	37
1	-4	24	20
1	-3	35	28
1	1	21	26
1	3	25	26
1	4	95	94
1	5	31	32
1	6	62	66
1	7	68	68
1	8	83	80
1	9	81	86
1	10	34	34
1	11	72	80
3	-8	17	26
3	-7	52	51
3	-6	88	92
3	-4	81	79
3	-3	60	57
3	-2	113	118
3	-1	23	24
3	2	12	6
3	3	63	60
H= 10			
0	-8	18	18
0	-6	44	40
0	-2	58	62
0	0	35	27
0	4	52	49
0	6	41	44
0	8	88	94
0	10	97	102
2	-8	47	49
2	-7	32	34
2	-6	34	33
2	-4	21	20
2	-2	65	59
2	0	28	31
2	1	76	74
2	2	46	48
2	3	116	107
2	5	60	56
2	6	28	23
2	7	30	24
2	8	36	40
H= 11			
1	-7	28	34
1	-3	70	65
1	0	46	43
1	2	71	68
1	3	45	42
1	4	89	91
1	5	31	33
H= 12			
0	-2	52	60
0	0	35	37

crystals were grown, and all were of the β form described here.

The intensities were estimated visually and were reduced to structure amplitudes by application of the Lorentz–polarization factor. No absorption corrections were made ($\mu = 17.8$ cm^{-1}), and the neglect of these, as well as the fact that the crystal was not uniformly bathed[25] in the incident beam, suggests that the quality of the X-ray data is not up to our usual standards. We report the results of the X-ray refinement for completeness, but we regard the neutron data as providing the definitive structure.

As with the α form, only the irradiated portion of the crystals, which were initially colorless, developed a deep red color which disappeared again on melting. There was no noticeable change in diffracted X-ray intensity associated with the color development. It has been previously observed[21] that irradiation at $-70°$ with an Hg arc also gives a red coloration to the crystals, which exhibit a six-line esr spectrum presumably due to (CO)$_5$Mn. This effect was not observed in the neutron experiment described below.

The structure was solved by the analysis of a three-dimensional Patterson function.[26] The y coordinate of the manganese atom was established as $^1/_4$ from the $0, 2y, {}^1/_2$ Harker line, but this special coordinate leads to ambiguity in the interpretation of the Patterson function in that the multiplicity of the $2x, 2y, 2z$ vector is then equal to that of the $^1/_2 - 2x, {}^1/_2, {}^1/_2 - 2z$ vector. The two possible solutions for the manganese atom position are related by $x_2 = {}^1/_4 - x_1$, $z_2 = {}^1/_4 - z_1$. The value of z was determined to be $^1/_8$ and, therefore, $z_2 = z_1$ for the two interpretations and the ambiguity reduces to the choice between x_1 or $^1/_4 - x_1$ for the x coordinate of the manganese atom. A difference Fourier synthesis, phased by the incorrect manganese position, clearly yielded the positions of the five carbon and five oxygen atoms insofar as they were correctly related to the incorrect position of the manganese atom. The octahedral structure was clear at this point, but the molecular packing was entirely unsatisfactory; there were O–O distances of 1.9 and 2.4 Å between molecules. The alternative placement of the manganese atom for which the magnitudes of the Mn contributions to the structure factors are unchanged leads to an identical molecular structure which packs satisfactorily into the unit cell. The structure was refined by full-matrix least-squares technique utilizing the 741 observed structure amplitudes, $|F_o|$. The quantity $\Sigma w(|F_o| - |F_c|)^2$ was minimized with the weighting scheme assigned as

$$\sigma(F_s) = \frac{100}{F_s} + 0.1F_s$$

where F_s is the observed structure factor on the scale presented in Table I and where $w = 1/\sigma^2(F_s)$. The atomic scattering factors used were those tabulated by Ibers[27] and the dispersion corrections were those tabulated by Templeton.[28] The dispersion corrections were applied to the calculated structure factors.[29] The data were not interscaled, but rather separate scale factors were refined for the individual layers. This is a justi-

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(25) The crystal length was greater than the diameter of the X-ray collimator and use of the tapered tip of the capillary caused the available diameter of the crystal to vary from 0.1 to 0.6 mm. This fact and the fact that the wall of the quartz capillary was not uniform in the tip led to certain errors in the data.

(26) The computer programs used in the structure analysis were all from the BNL crystallographic program library: LPFPRE for precession data processing, FORDAP for Patterson and Fourier calculations, LINUS for least-squares refinements, and ORTEP and ORFFE for structure description.

(27) J. A. Ibers, "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1-A.

(28) D. H. Templeton, ref 27, Table 3.3.2-A.

(29) J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

fied procedure, even with a total anisotropic refinement, because of the distribution of various classes of reflections among the layers. The anisotropic refinement of the manganese, carbon, and oxygen atoms (with the hydrogen atom position and thermal parameters fixed from the neutron refinement below) resulted in an R ratio

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

of 0.086. A difference Fourier synthesis, with the hydrogen atom excluded, based on only the averaged independent reflections, exhibited a few peaks as high as 0.65 e$^-$/Å^3 and no indication of the hydrogen atom position.

In Table II the final positional parameters from the anisotropic refinement are given. In Table III the corresponding thermal parameters are given and Table IV gives the root-mean-squares amplitudes of vibration of the atoms. In Table I the values of $|F_o|$ and $|F_c|$ in electrons are given for the independent reflections. The values of $|F_o|$ tabulated are average values in those cases where there was more than one observation. The values of R_1 and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$ for the data of Table I are 0.086 and 0.117, respectively. The error in an observation of unit weight is 0.75.

TABLE II

POSITIONAL PARAMETERS FOR β-HMn(CO)$_5$[a]

Atom	x	y	z
Mn	0.0785 (7)	0.2596 (17)	0.1257 (5)
	0.0771 (2)	0.2566 (3)	0.1258 (1)
C$_1$	0.1240 (4)	0.3760 (10)	0.0448 (3)
	0.1241 (16)	0.3769 (22)	0.0458 (9)
O$_1$	0.1494 (7)	0.4534 (15)	−0.0059 (4)
	0.1491 (12)	0.4561 (18)	−0.0039 (6)
C$_2$	−0.0440 (5)	0.1182 (11)	0.0853 (3)
	−0.0424 (13)	0.1197 (22)	0.0848 (8)
O$_2$	−0.1173 (7)	0.0299 (14)	0.0671 (5)
	−0.1177 (10)	0.0339 (19)	0.0628 (7)
C$_3$	0.1891 (5)	0.3661 (10)	0.1823 (3)
	0.1864 (16)	0.3682 (23)	0.1823 (9)
O$_3$	0.2538 (7)	0.4335 (14)	0.2189 (4)
	0.2563 (10)	0.4330 (18)	0.2169 (7)
C$_4$	−0.0117 (5)	0.4776 (12)	0.1523 (3)
	−0.0128 (14)	0.4757 (25)	0.1535 (10)
O$_4$	−0.0677 (7)	0.6091 (16)	0.1715 (4)
	−0.0676 (10)	0.6061 (19)	0.1706 (8)
C$_5$	0.1539 (5)	0.0052 (11)	0.1207 (3)
	0.1582 (13)	0.0037 (19)	0.1212 (8)
O$_5$	0.1989 (6)	−0.1540 (15)	0.1186 (4)
	0.1989 (10)	−0.1510 (15)	0.1199 (7)
H	0.0363 (10)	0.1553 (22)	0.1958 (7)
	...	...	...

[a] For each atom, the neutron result is given on the first line and the X-ray result on the second. Numbers in parentheses here and in subsequent tables are estimated standard deviations in the least significant figures.

TABLE III

ANISOTROPIC THERMAL PARAMETERS (×10^4) FOR β-HMn(CO)$_5$

Atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	33 (6)	139 (3)	17 (3)	20 (12)	−7 (4)	8 (9)
	39 (2)	146 (4)	12 (1)	8 (2)	2 (1)	−1 (2)
C$_1$	48 (4)	180 (21)	15 (2)	−12 (8)	−7 (2)	2 (5)
	55 (14)	180 (37)	23 (4)	5 (16)	0 (10)	−5 (12)
O$_1$	69 (6)	302 (31)	20 (3)	−19 (11)	−5 (3)	25 (7)
	73 (13)	315 (35)	19 (3)	2 (15)	−6 (7)	37 (9)
C$_2$	47 (4)	213 (23)	27 (2)	−15 (9)	−2 (3)	−13 (6)
	35 (10)	225 (38)	17 (4)	8 (16)	0 (9)	−10 (12)
O$_2$	67 (7)	262 (28)	39 (3)	−43 (12)	−10 (4)	−21 (8)
	39 (8)	310 (33)	37 (5)	−19 (13)	−6 (9)	−15 (11)
C$_3$	55 (4)	207 (22)	16 (2)	22 (9)	−10 (3)	−4 (5)
	67 (15)	184 (39)	16 (4)	12 (18)	−4 (10)	26 (12)
O$_3$	92 (7)	300 (29)	26 (3)	21 (12)	−24 (4)	−40 (7)
	49 (9)	330 (35)	32 (4)	−14 (14)	−11 (9)	−35 (12)
C$_4$	45 (4)	192 (23)	21 (2)	9 (8)	−1 (2)	−13 (6)
	47 (12)	255 (43)	27 (5)	27 (18)	13 (11)	−27 (13)
O$_4$	85 (7)	330 (32)	30 (3)	45 (14)	−3 (4)	−23 (8)
	57 (10)	328 (36)	40 (5)	66 (15)	11 (9)	−17 (12)
C$_5$	48 (3)	148 (19)	19 (2)	8 (8)	−4 (2)	4 (5)
	58 (14)	148 (35)	17 (4)	7 (14)	−4 (9)	7 (10)
O$_5$	79 (6)	186 (26)	32 (3)	10 (12)	2 (3)	14 (7)
	72 (10)	154 (25)	36 (4)	15 (12)	4 (8)	−10 (10)
H	96 (9)	288 (46)	24 (4)	25 (18)	5 (5)	7 (11)
	...	...	...	...	...	...

[a] The general anisotropic temperature factor has the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE IV

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)

Atom	Min	Intermed	Max
Mn	0.113 (22)	0.183 (16)	0.197 (13)
	0.148 (4)	0.165 (4)	0.180 (3)
C$_1$	0.153 (11)	0.184 (12)	0.212 (9)
	0.186 (20)	0.203 (30)	0.213 (26)
O$_1$	0.172 (14)	0.219 (11)	0.269 (11)
	0.146 (20)	0.236 (20)	0.276 (15)
C$_2$	0.173 (13)	0.208 (11)	0.237 (10)
	0.160 (25)	0.174 (26)	0.219 (19)
O$_2$	0.167 (16)	0.261 (12)	0.286 (12)
	0.161 (23)	0.245 (17)	0.277 (17)
C$_3$	0.147 (14)	0.190 (12)	0.235 (9)
	0.190 (22)	0.201 (32)	0.237 (30)
O$_3$	0.145 (17)	0.236 (12)	0.319 (12)
	0.158 (30)	0.231 (20)	0.292 (16)
C$_4$	0.175 (14)	0.182 (9)	0.220 (10)
	0.129 (39)	0.228 (27)	0.259 (22)
O$_4$	0.208 (15)	0.235 (12)	0.298 (13)
	0.147 (22)	0.279 (23)	0.290 (18)
C$_5$	0.160 (12)	0.184 (10)	0.204 (8)
	0.159 (23)	0.187 (23)	0.213 (28)
O$_5$	0.184 (14)	0.243 (11)	0.254 (12)
	0.168 (15)	0.235 (17)	0.265 (17)
H	0.209 (16)	0.230 (19)	0.279 (15)
	...	...	...

The Neutron Structure

Crystals were grown as described above and were examined for quality and orientation by taking X-ray photographs on the precession cameras. They were then transferred in a liquid nitrogen bath to a four-circle diffractometer at the Brookhaven high-flux beam reactor where they were cooled during data collection by a temperature-controlled cold nitrogen stream from ALTA.[30] The temperature was maintained at approximately −105° while data were obtained using a θ–2θ step scan technique with $\Delta(2\theta) = 0.1°$. No phase transition was observed between room temperature and −160°. Moreover, the cell constants at −105° appear to be insignificantly different from those obtained at −75°, at least as judged from our ability to locate the diffracted neutron beams. Accordingly, the X-ray cell was used in the interpretation of the neutron data.

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(30) R. Rudman and J. B. Godel, *J. Appl. Cryst.*, in press.

Table V

Observed and Calculated Neutron Structure Amplitudes (in Units of 10^{-12} cm) for β-$HMn(CO)_5$

K	L	FOBS	FCALC
H= 0			
0	6	58	55
0	8	134	130
0	10	15	10
0	12	100	100
0	14	18	22
0	16	100	99
0	18	23	22
0	20	58	58
0	22	18	13
2	1	52	52
2	2	34	31
2	3	13	13
2	4	163	162
2	6	15	18
2	7	22	21
2	8	116	115
2	9	27	30
2	11	38	42
2	12	106	101
2	13	34	33
2	14	22	27
2	18	22	23
2	20	52	53
2	24	29	28
4	0	60	66
4	1	14	14
4	3	51	49
6	0	41	40
H= 1			
1	-25	18	18
1	-23	42	40
1	-21	31	28
1	-17	22	23
1	-15	64	66
1	-13	42	46
1	-11	84	87
1	-10	36	34
1	-9	45	47
1	-8	14	15
1	-7	113	117
1	-6	239	239
1	-5	88	89
1	-2	28	31
1	-1	57	48
1	0	44	45
1	1	163	184
1	2	32	35
1	3	60	79
1	4	33	24
1	8	40	42
1	9	83	86
1	15	14	23
1	17	66	67
1	18	21	22
1	19	19	6
1	20	20	16
1	21	45	46
1	23	17	4
1	25	27	31
3	-23	21	23
3	-21	16	10
3	-20	18	17
3	-19	55	56
3	-17	30	28
3	-15	62	62
3	-14	18	18
3	-11	89	92
3	-10	13	16
3	-7	97	97
3	-4	18	19
3	-3	71	71
3	-1	61	57
3	0	18	18
3	1	95	95
3	3	23	15
3	5	199	201
3	8	29	29
3	9	89	86
3	23	15	11
5	-3	71	76
5	-1	33	18
5	1	85	84
7	-3	38	43
7	-2	16	15
7	-1	13	5
7	0	15	12
7	1	38	39
7	3	15	10
H= 2			
0	-26	24	24
0	-24	22	22
0	-22	43	41
0	-20	34	34
0	-18	36	36
0	-16	18	7
0	-14	114	109
0	-10	124	112
0	-8	22	26
0	-6	162	159
0	0	71	63
0	6	219	196
0	8	26	25
0	10	209	201
0	12	18	22
0	20	15	9
0	22	43	44
0	24	22	21
2	-22	19	23
2	-20	33	31
2	-18	49	50
2	-17	15	16
2	-16	53	51
2	-12	77	80
2	-9	46	43
2	-8	82	86
2	-7	12	5
2	-6	83	88
2	-5	11	3
2	-3	15	11
2	-2	155	139
2	-1	218	215
2	0	85	86
2	10	32	36
2	12	33	46
2	13	18	14
2	17	21	21
2	20	35	29
2	21	15	12
2	22	31	28
4	-20	18	20
4	-18	36	40
4	-16	39	40
4	-14	34	35
4	-12	41	43
4	-11	24	25
4	-10	51	53
4	-9	20	22
4	-8	52	49
4	-6	91	84
4	-5	39	39
4	-4	83	77
4	-3	17	18
4	0	57	61
4	2	86	82
4	3	52	49
4	4	33	39
4	6	115	100
4	8	56	56
4	10	74	73
4	12	46	48
4	13	26	26
4	14	25	33
6	-2	24	31
6	-1	16	15
6	0	33	35
6	1	23	21
6	2	20	24
6	3	20	21
8	-2	22	29
H= 3			
1	-25	19	17
1	-19	46	44
1	-17	44	42
1	-15	51	48
1	-14	20	23
1	-13	69	66
1	-12	41	41
1	-11	99	104
1	-10	42	44
1	-9	51	50
1	-7	186	196
1	-6	44	45
1	-5	81	78
1	-3	153	162
1	-2	44	41
1	-1	129	119
1	0	32	32
1	1	155	149
1	2	53	52
1	3	108	82
1	4	242	229
1	5	107	123
1	9	77	86
1	10	32	29
1	12	28	25
1	13	82	78
1	14	22	15
1	15	59	61
1	17	57	59
1	19	34	30
1	21	29	30
1	22	20	20
1	23	24	21
1	25	23	25
3	-21	18	19
3	-19	41	39
3	-17	25	23
3	-15	72	74
3	-13	20	20
3	-11	73	68
3	-10	55	55
3	-8	23	21
3	-7	24	22
3	-6	17	16
3	-5	79	76
3	-4	22	28
3	-3	92	90
3	-2	36	36
3	-1	68	65
3	0	30	31
3	1	90	90
3	2	18	18
3	3	85	75
3	4	15	19
3	5	82	77
3	6	32	42
3	7	46	43
3	11	74	70
3	13	40	49
3	14	17	17
3	17	25	26
3	19	36	33
3	21	35	33
5	-19	32	32
5	-17	20	22
5	-15	34	33
5	-13	31	30
5	-9	30	33
5	-5	31	33
5	-4	35	34
5	-3	26	30
5	-2	19	22
5	-1	27	28
5	1	40	42
5	2	15	15
5	5	49	51
5	7	72	70
5	9	43	42
5	11	20	20
5	13	22	20
7	-3	27	31
7	-1	33	30
7	0	10	6
7	1	28	27
7	3	20	22
H= 4			
0	-2	168	139
0	0	88	93
0	2	145	127
2	-22	35	37
2	-18	60	61
2	-17	15	10
2	-15	19	18
2	-13	14	18
2	-12	28	29
2	-10	98	95
2	-9	22	23
2	-8	24	23
2	-7	15	16
2	-6	122	121
2	-4	47	48
2	-3	19	19
2	-2	197	208
2	-1	28	28
2	4	47	50
2	5	11	11
2	6	112	105
2	7	28	23
2	8	35	35
2	9	20	17
2	10	77	72
2	12	45	44
2	19	16	11
2	20	16	17
2	22	36	36
4	-18	41	40
4	-16	29	28
4	-14	47	49
4	-12	22	24
4	-10	28	25
4	-9	14	10
4	-8	38	37
4	-7	20	18
4	-6	64	59
4	-4	28	20
4	-3	18	15
4	-2	107	101
4	-1	35	32
4	0	46	46
4	1	27	29
4	2	121	115
4	4	54	49
4	6	83	84
4	8	38	40
4	10	57	57
4	16	30	29
4	18	46	40
6	-18	31	34
6	-17	16	15
6	-14	36	38
6	-13	15	17
6	-10	56	55
6	-6	65	60
6	-5	20	22
6	-3	21	18
6	-2	55	55
6	0	17	14
6	1	14	11
6	2	51	58
6	4	16	18
6	5	42	42
6	7	20	19
6	8	16	13
6	10	37	41
6	11	18	15
6	18	27	24
8	-2	16	15
H= 5			
1	-1	108	114
1	1	42	29
1	3	190	189
3	-21	27	31
3	-19	16	1
3	-17	47	48
3	-15	20	9
3	-13	41	45
3	-11	16	5
3	-9	71	79
3	-8	22	23
3	-7	29	27
3	-5	137	136
3	-4	56	60
3	-3	20	20
3	-2	28	26
3	-1	130	125
3	0	55	57
3	2	18	11
3	3	42	47
3	6	23	19
3	7	99	96
3	10	25	28
3	11	45	44
3	12	21	23
3	15	51	52
5	-14	15	14
5	-13	46	46
5	-12	14	16
5	-9	33	35
5	-7	17	16
5	-6	15	11
5	-5	55	53
5	-3	14	9
5	-2	20	19
5	-1	59	60
5	8	24	25
5	10	18	17
5	11	45	45
5	14	20	21
5	15	31	32
7	-13	27	22
7	-9	36	34
7	-5	25	24
7	-1	29	28
7	0	11	6
7	7	43	39
7	11	26	23
H= 6			
0	-2	74	73
0	0	102	108
0	2	13	16
2	-3	64	59
2	-2	15	8
2	0	108	112
2	1	14	17
2	2	56	54
2	3	48	41
4	-22	13	14
4	-20	27	26
4	-6	15	17
4	-5	19	15
4	-4	87	81
4	-3	16	17
4	-2	20	21
4	-1	23	26
4	0	53	53
4	1	21	21
4	2	21	20
4	3	15	16
4	5	15	19
4	8	42	42
4	12	58	62
4	16	39	39
4	20	31	31
6	-10	14	11
6	-8	39	39
6	-4	50	49
6	-3	18	14
6	-2	16	11
6	0	66	60
6	1	25	27
6	4	53	48
6	8	50	43
6	11	22	23
8	-4	17	13
8	0	30	16
H= 7			
1	-1	20	13
1	0	13	13
1	1	77	80
1	2	56	61
1	3	42	39
3	-3	70	65
3	-2	19	19
3	-1	61	70
3	1	83	85
3	2	24	6
3	3	57	52
5	-19	22	22
5	-17	21	20
5	-15	25	26
5	-13	20	23
5	-12	16	17
5	-11	35	37
5	-9	34	34
5	-5	43	46
5	-3	61	65
5	-2	26	26
5	-1	36	37
5	0	12	10
5	2	22	9
5	3	22	14
5	8	18	14
5	11	26	28
5	12	22	20
5	13	27	28
5	15	17	19
5	17	20	22
5	19	11	12
7	-3	25	19
7	-1	25	13
7	1	23	30
H= 8			
0	-2	38	43
0	0	53	54
0	2	84	92
2	-3	30	31
2	-2	71	74
2	0	103	106
2	2	58	66
4	-2	31	31
4	-1	16	11
4	1	30	30
6	-14	19	16
6	-12	14	14
6	-10	19	20
6	-8	20	20
6	-6	28	21
6	-5	18	16
6	-4	20	24
6	-3	22	23
6	-2	26	25
6	0	26	25
6	2	24	22
6	4	30	31
6	6	28	26
6	8	22	13
6	10	24	24
6	12	14	15
H= 9			
1	-2	21	11
1	-1	27	30
1	0	13	16
1	1	61	69
1	2	28	16
1	3	43	43
3	-3	46	46
3	-2	31	28
3	-1	24	25
3	1	61	59
5	-3	34	36
5	-1	22	21
5	3	24	26
7	-3	24	29
7	1	23	26
7	5	21	17
H= 10			
0	-2	93	88
0	2	76	83
2	-3	19	9
2	-2	56	51
2	-1	13	13
2	0	21	23
2	2	50	52
2	3	47	50
4	-3	21	5
4	-2	56	56
4	-1	19	19
4	1	19	4
4	2	42	53
6	-2	23	21
6	1	17	12
H= 11			
1	0	28	18
1	1	17	18
1	2	21	23
1	3	52	54
3	-1	38	34
3	0	14	4
3	3	49	49
5	1	16	13
5	3	29	32
H= 12			
0	-2	41	42
0	0	41	40
2	-1	14	8
2	0	34	33
2	2	18	23
4	-3	15	5
4	-2	29	28
4	-1	16	5
4	2	23	34
6	-2	13	10
H= 13			
1	-3	29	29
1	0	15	18
1	1	22	22
1	3	25	23
3	-3	30	30
3	-2	16	8
3	-1	38	37
3	0	13	1
3	1	36	38
3	3	31	30
5	3	17	17
H= 14			
0	-2	19	17
0	0	35	29
2	-2	18	12
2	0	32	28
2	1	14	16
2	2	16	15
2	3	18	16
4	-2	20	16
H= 15			
1	-3	25	22
1	-2	20	18
1	-1	11	11
1	1	31	28
1	2	18	13
3	-3	27	33
H= 16			
0	-2	29	24
0	2	33	36
2	-2	30	28
2	2	18	23

The incident beam was obtained by monochromatization by the (331) reflection of a single crystal of germanium; thus there was no $\lambda/2$ contamination in the incident beam. The nominal wavelength was 1.073 Å with a spread of about 1%. Scattered neutrons were counted using a $^{10}BF_3$ counter with a slit width large enough to accept the divergence of the incident beam. All data were collected from a single cylindrical crystal 1 mm in diameter and 3.5 mm high. The absence of data for which $h > 12$ was caused by a failure of the low-temperature system with subsequent melting of the crystal. F^2 values were obtained from the integrated intensities by multiplication by sin 2θ. No correction was made for absorption ($\mu = 0.23\ \text{cm}^{-1}$).

Starting with parameters for the manganese, carbon, and oxygen atoms from the X-ray refinement and a hydrogen atom placed at a distance of 1.45 Å from manganese along the pseudofourfold axis of the molecule, a series of least-squares refinements led to the final positional parameters in Table II, the thermal parameters of Table III, and the calculated structure factors of Table V. In the full-matrix least-squares refinement the weights used were based on the estimated standard deviation

$$\sigma(F^2) = [\sigma^2_{\text{counting}} + (0.10F^2)^2]^{1/2}$$

where $\sigma^2_{\text{counting}}$ is derived from the assumption of standard Poisson statistics. The refined isotropic extinction parameter[31] corresponds to a mosaic spread parameter of approximately 30 sec or a domain size of 0.2 μ depending upon whether a Zachariasen[32] type I or type II description is chosen. The calculated structure factors of Table V have been multiplied by the extinction correction

$$E = \left[1 + \frac{2\bar{T}F_c^2g\lambda^3}{V^2 \sin 2\theta}\right]^{-1/4}$$

where F_c^2 is on an absolute scale, λ is in Å, the cell volume V is in Å^3, $\bar{T} = 0.1$ cm is the average path length in the crystal, and g (the refined extinction parameter) has the value 1930. The neutron scattering lengths used were: Mn, −0.370; H, −0.378; C, 0.665; O, 0.578 × 10^{-12} cm. The values of R_1, R_2, and the error in an observation of unit weight for this refinement are 0.062, 0.080, and 1.45, respectively. An analysis of the weighted errors at the end of this refinement revealed no significant dependency on θ or intensity.

The general agreement between the X-ray and neutron results on β-$HMn(CO)_5$ is very satisfactory. In particular, the agreement exhibited among the thermal

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(31) P. Coppens and W. C. Hamilton, *Acta Cryst.*, in press.

(32) W. H. Zachariasen, *ibid.*, **23**, 558 (1968).

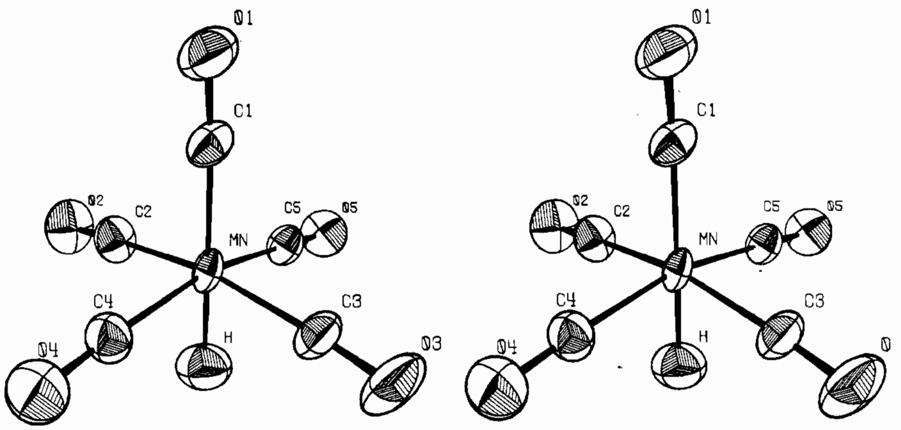

Figure 1.—A stereoscopic drawing of the molecular structure of β-$HMn(CO)_5$.

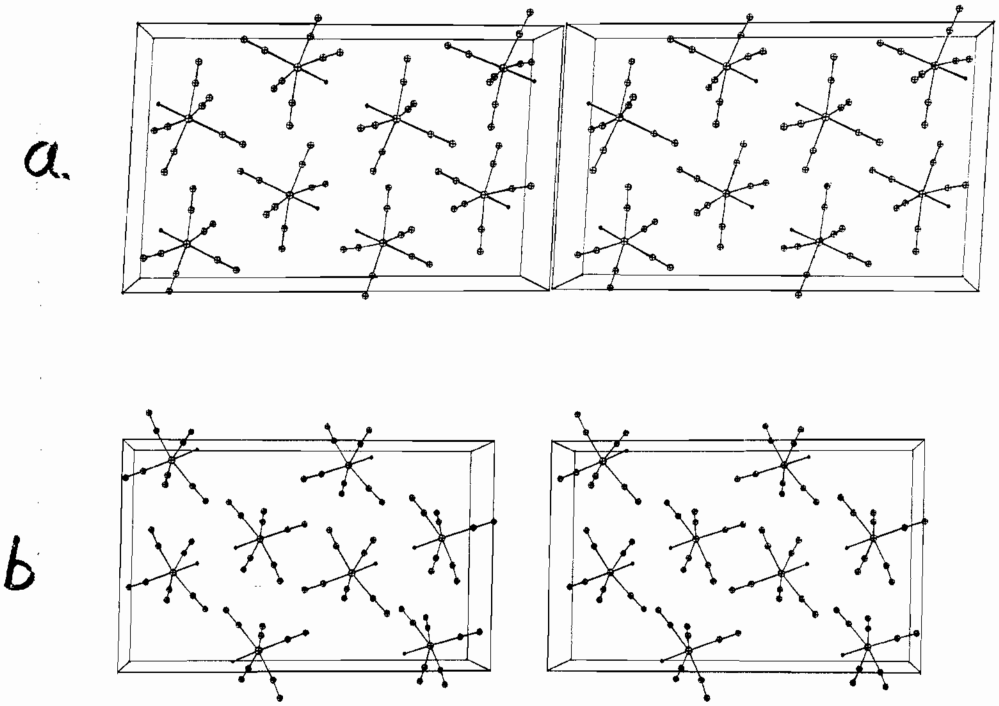

Figure 2.—Stereoscopic views of the unit cells of (a) α-$HMn(CO)_5$ and (b) β-$HMn(CO)_5$. In both views the *a* axis runs from top to bottom, the *c* axis from left to right, and the *b* axis, down which the view is prepared, runs into the paper.

parameters indicates that the X-ray data are reasonably free from systematic errors and that anisotropic refinement of these data was justified.

Table IV gives the root-mean-square amplitudes of vibration that may be calculated from the neutron diffraction data. An indication of the directions of the principal axes of vibration may be obtained from Figure 1. In general these vibrations seem reasonable.

Description of the Crystal Structure and Comparison with α-$HMn(CO)_5$

The crystal structure of β-$HMn(CO)_5$ consists of the packing of well-separated monomeric units. Each of these units has approximate symmetry C_{4v} as discussed in the next section. Stereoscopic views of the unit cells of both the α and β forms are given in Figure 2. The packing of the two forms is very different, although pairs of molecules with adjacent H···H contacts are present in both structures. The H···H separation in the β form is 2.29 Å, whereas if one assumes that the H atom is on the pseudofourfold axis at a distance from the Mn atom of 1.600 Å in the α form, this contact is 2.23 Å. Thus the H···H interaction is that expected from the van der Waals radius of hydrogen. The arrangement of the Mn–H···H–Mn geometries in the two forms is nearly identical, so that no complications result in the interpretation of the broad-line nmr data owing to uncertainty about which of the forms was studied. The closest Mn···Mn separations are 5.17 and 5.21 Å in the α and β forms. In the α form the angle between the pseudofourfold axes of the separate molecules whose hydrogen atoms are in van der Waals contact is approximately 135° and these fourfold axes lie nearly in the $(\bar{4}03)$ plane. In the β form the angle is approximately 132° and these axes lie nearly in the (503) plane. In both substances there are 16 O···O

TABLE VI

SELECTED BOND DISTANCES (Å) AND ANGLES (DEG)

	Neutron	X-Ray		Neutron	X-Ray
Mn–H	1.601 (16)	. . .	C_1–O_1	1.143 (9)	1.131 (19)
Mn–C_1	1.822 (12)	1.824 (17)	C_2–O_2	1.121 (9)	1.137 (18)
Mn–C_2	1.888 (13)	1.853 (16)	C_3–O_3	1.129 (10)	1.144 (20)
Mn–C_3	1.844 (13)	1.843 (19)	C_4–O_4	1.138 (9)	1.111 (17)
Mn–C_4	1.835 (12)	1.843 (15)	C_5–O_5	1.141 (9)	1.091 (16)
Mn–C_5	1.845 (12)	1.87 (13)	H···H	2.291 (25)	. . .
			Mn···Mn	5.212 (19)	5.194 (4)
Mn–C_1–O_1	177.6 (7)	177.0 (18)	C_2–Mn–C_3	167.4 (6)	168.7 (7)
Mn–C_2–O_2	176.9 (8)	176.6 (15)	C_2–Mn–C_4	89.8 (5)	90.3 (7)
Mn–C_3–O_3	177.2 (7)	178.0 (15)	C_2–Mn–C_5	87.7 (5)	89.7 (6)
Mn–C_4–O_4	177.2 (7)	179.2 (18)	C_2–Mn–H	83.9 (7)	. . .
Mn–C_5–O_5	178.4 (7)	175.0 (14)	C_3–Mn–C_4	89.7 (5)	88.2 (7)
C_1–Mn–C_2	94.9 (5)	94.9 (7)	C_3–Mn–C_5	89.3 (5)	88.7 (7)
C_1–Mn–C_3	97.7 (5)	96.4 (7)	C_3–Mn–H	83.5 (7)	. . .
C_1–Mn–C_4	97.8 (5)	97.8 (8)	C_4–Mn–C_5	164.0 (6)	164.3 (7)
C_1–Mn–C_5	98.2 (5)	97.8 (7)	C_4–Mn–H	82.1 (6)	. . .
C_1–Mn–H	178.8 (8)	. . .	C_5–Mn–H	81.9 (7)	. . .

TABLE VII

LEAST-SQUARES PLANES

Plane no.[a]	*A*	*B*	*C*	*D*
1	6.937	−5.037	−3.629	−1.206
	6.953	−5.020	−3.783	−1.227
2	9.302	2.633	9.150	2.545
	9.244	2.653	9.244	2.557
3	4.138	2.557	−16.535	−1.319
	4.211	2.608	−16.405	−1.286

Plane 1			Plane 2		
	Distance from plane, Å			Distance from plane, Å	
Atom	Neutron	X-Ray	Atom	Neutron	X-Ray
Mn	−0.013 (10)	−0.001 (2)	Mn	0.018 (10)	0.000 (2)
C_1	0.010 (6)	0.025 (16)	C_1	0.009 (5)	0.014 (17)
O_1	−0.020 (8)	−0.011 (13)	O_1	−0.016 (8)	−0.005 (13)
C_2	−0.004 (6)	0.011 (14)	C_4	−0.003 (6)	0.005 (18)
O_2	0.009 (9)	0.001 (13)	O_4	−0.002 (8)	0.003 (14)
C_3	0.013 (6)	−0.015 (16)	C_5	0.004 (6)	0.036 (16)
O_3	−0.011 (8)	0.015 (12)	O_5	−0.015 (8)	−0.010 (12)
H	−0.035 (13)		H	−0.007 (14)	. . .

Plane 3		
	Distance from plane, Å	
Atom	Neutron[b]	X-Ray
C_2	+0.029 (6)	0.028 (15)
C_3	+0.025 (6)	0.040 (17)
C_4	−0.026 (6)	−0.045 (19)
C_5	−0.025 (6)	−0.027 (15)

[a] The planes are of the form $Ax + By + Cz - D = 0$ where x, y, and z are the fractional coordinates of the atoms in the monoclinic cell. The neutron results are on the first line and the X-ray results are on the second. [b] Manganese is displaced 0.24 Å from this plane toward C_1.

contacts less than 3.5 Å in length, the shortest interaction in the α form being 3.10 Å and that in the β form being 3.13 Å. On this basis it is reasonable to assume that the difference between these two "pseudodimer" packing arrangements is small and that minor perturbations, for example the presence of small amounts of an impurity in one of the preparations, may be responsible for the different arrangements. The effects on a crystal structure of small amounts of impurities are well known. To take but one example Smith[33] has pointed out that the crystal structures of the even, normal paraffins in the C_{18}–C_{30} range are markedly changed by the presence of a few per cent of neighboring homologs.

Description of the Molecular Structure

Molecules of β-$HMn(CO)_5$ have nearly C_{4v} symmetry and exhibit no significant deviations from the geometry found in α-$HMn(CO)_5$ (see Figure 1). Principal intramolecular bond distances and angles are given in Table VI. Table VII lists some of the weighted least-squares planes that can be put through a molecule of β-$HMn(CO)_5$.

The availability of both neutron data, for which the scattering amplitude of carbon is greater than that of oxygen, and X-ray data (the situation being reversed) provides an unusual opportunity to test the hypothesis that Mn–O–C as opposed to the expected Mn–C–O linkages exist in this compound. Least-squares refinement of this reversed model (a) for the neutron case gave $R_1 = 0.067$ and $R_2 = 0.087$ with insignificant shifts in the positional parameters and as anticipated, large shifts in the thermal parameters, the largest being associated with the –C–O bond direction, and (b) for the X-ray case ($R_1 = 12.6$, $R_2 = 15.8$) gave unexpectedly large positional shifts of 0.02–0.21 Å in the direction of oxygen as well as large amplitudes of apparent thermal motion along the –C–O bond. In addition the thermal parameters for each of the oxygen atoms are physically unrealistic. Both the positional and thermal parameters of Mn and H for both data sets are pleasingly unchanged. The reasonableness and consistency of the bond lengths and thermal parameters as well as the better agreement factors observed for the Mn–C–O case leave little doubt that the metal to carbonyl bonding is through an Mn–C bond rather than an Mn–O bond.

The axial Mn–C distance (*trans* to H) of 1.822 (12) Å does not differ significantly from the mean of the four equatorial Mn–C distances (1.853 (12) Å). [The standard deviation of the mean here and elsewhere in the paper is based on the external estimate.] Yet the results from a series of $XMn(CO)_5$ complexes, given in Table VIII, indicate a general shortening of the axial Mn–C distance. The consistency among the results from compounds with widely differing X groups suggests that there is no unusual geometrical "*trans* effect"

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[33] A. E. Smith, *J. Chem. Phys.*, **21**, 2229 (1953).

TABLE VIII

AXIAL *vs.* EQUATORIAL Mn–C BOND LENGTHS (Å) IN $XMn(CO)_5$ COMPLEXES

Compound	Technique	Mn–C_{ax}	Mn–C_{eq}	Eq–Ax	Ref
α-$HMn(CO)_5$	X-Ray	1.821 (9)	1.840 (5)	0.019 (10)	*a*
β-$HMn(CO)_5$	X-Ray	1.824 (17)	1.853 (7)	0.029 (18)	*b*
β-$HMn(CO)_5$	Neutron	1.822 (12)	1.853 (12)	0.031 (17)	*b*
$(CO)_5Mn–Mn(CO)_5$	X-Ray	1.792 (14)	1.831 (9)	0.039 (17)	*c*
$(CO)_5Mn–Fe(CO)_4–Mn(CO)_5$	X-Ray	1.805 (10)[e]	1.855 (10)[e]	0.050 (14)	*d*

[a] Reference 2. [b] This work. [c] L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963). [d] P. A. Agron, R. D. Ellison, and H. A. Levy, *ibid.*, **23**, 1079 (1967). [e] Estimated error.

for the H ligand. In all of these complexes the equatorial carbonyl groups bend down toward the X group and away from the axial carbonyl group. The mean C–O bond length of 1.134 (4) Å derived from this "equal atom" neutron study should more realistically reflect its value when compared with that derived from typical "heavy-atom" carbonyl complexes determined by X-rays. A distance of 1.137 (2) Å was obtained for the gas-phase electron diffraction study of $HMn(CO)_5$.[19a]

X-Ray diffraction data do not lead to precise metal–hydrogen bond lengths, especially in substances with small unit cells. On the other hand, the scattering amplitude for neutrons of H is nearly equal to that of Mn and is only slightly less than the scattering lengths of C and O. Accordingly, there is no difficulty in locating the H atom in β-$HMn(CO)_5$ to reasonably high precision from the neutron diffraction data. Thus in Figure 3 we show the scattering density in one of the planes through the molecule. Note that the Mn and H positions are very well defined. (These regions are negative because of the negative scattering amplitudes of H and Mn.) In the present study we have located the hydrogen atom to a precision of 0.01 Å. We have thus established beyond any doubt the fact that the hydrogen atom in β-$HMn(CO)_5$ is a well-behaved ligand that occupies the sixth coordination site in a C_{4v} distorted octahedron about Mn. The bond length of 1.601 (16) Å is in reasonable agreement with that which can be predicted from the sums of covalent radii (0.3[34] or 0.2 Å[35,36] for H and 1.39 Å[37] for Mn). Thus it seems certain that the Mn–H bond in this compound is a normal covalent bond. This distance found here also adds credence to earlier reports of (a) an average value of 1.65 (10) Å for the five independent bridging Mn–H distances in $HMn_3(CO)_{10}(BH_3)_2$,[38] (b) an Rh–H distance of 1.60 (12) Å in $RhH(CO)(P(C_6H_5)_3)_3$,[7] and (c) a linear symmetric bridge in the $(CO)_5CrHCr(CO)_5^-$ ion[35] where the Cr–Cr distance is 3.41 Å.

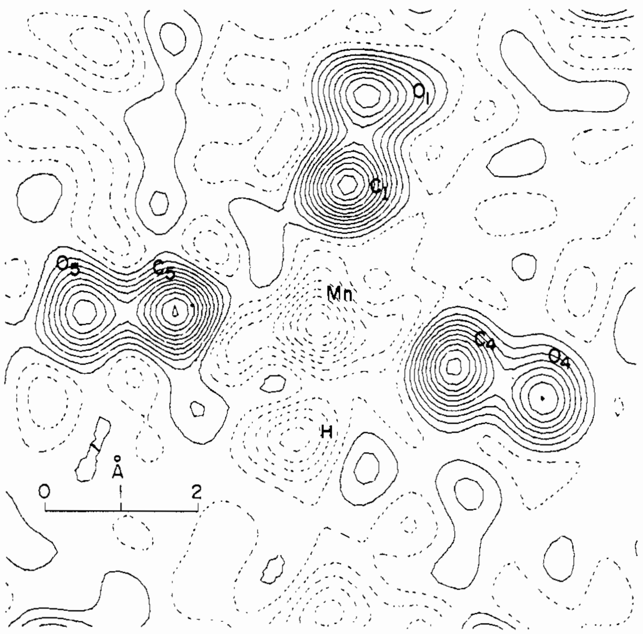

Figure 3.—A map of neutron scattering density through one of the planes of the β-$HMn(CO)_5$ molecule. The contour interval is 1.190 F/Å^3 (1 Fermi = 10^{-13} cm^{-1}) with the first positive contour at 0.595 F/Å^3. A difference Fourier in this plane had a residual density ranging from +0.39 to −0.38 F/Å^3.

Since there seems at present no satisfactory explanation of the anomalously short Mn–H bond length predicted by the broad-line proton nmr experiment, one should exhibit skepticism regarding those metal–hydrogen distances obtained by application of the present theory to systems containing quadrupolar nuclei.

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(34) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 226.

(35) L. B. Handy, P. M. Treichel, L. F. Dahl, and R. G. Hayter, *J. Am. Chem. Soc.*, **88**, 336 (1966), by use of an empirical value of 0.2 Å for the hydrogen radius and half the metal–metal bond length[36] in a number of transition metal complexes have been able to predict a reasonably self-consistent set of M–H distances (1.65 Å for Mn–H).

(36) R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2576 (1965), and references cited therein.

(37) F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, **5**, 1851 (1966).

(38) H. D. Kaesz, W. Fellmann, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2753 (1965).