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The Crystal Structure of *cis*-N-Methylcarboxamido Methylamine Tetracarbonyl Manganese(I), $Mn(CO)_4(NH_2CH_3)(CONHCH_3)$*

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A single-crystal x-ray structure analysis of one form of a compound with empirical formula $MnC_7H_9O_5N_2$, previously postulated to be seven-coordinated, has been completed. The crystals are tetragonal, space group $I4_1/a$, 16 molecules per unit cell, with unit cell dimensions $a=b=19.91\pm0.05$ and $c=11.90\pm0.05$ Å, and a calculated density of 1.45 g/cm^3. Using three-dimensional scintillation-counter data and a full matrix anisotropic least-squares analysis, the refinement of all non-hydrogen atoms has yielded a final unweighted reliability index of 9.5% for 1315 observed reflections. The configuration about the manganese atom is approximately octahedral, the ligands being four carbonyl groups, one methylamine group, and one N-methylcarboxamido group. The manganese-carbonyl distances are of two types, 1.847 ± 0.011 and 1.775 ± 0.013 Å. The shorter distance occurs trans *to the methylamine group. The N-methylcarboxamido group is planar, due to partial double bond character of the C–N bond. All other bond distances and angles are reasonable when van der Waals interactions are considered.*

Introduction

A compound with empirical formula $MnC_7H_9O_5N_2$ has recently been prepared and infrared and nuclear magnetic resonance studies have led to the postulated structure $Mn(CO)_5(NHCH_3)(NH_2CH_3)$, all seven groups being directly bonded to the central manganese atom.[1] Because of the uniqueness of the proposed structure, an x-ray crystallographic investigation was undertaken to obtain an unambiguous answer. The compound was found to crystallize into two crystal systems: monoclinic and tetragonal. The structure of the tetragonal form has been determined and is described below.

Experimental Section

Crystals of this compound were kindly supplied to us by Dr. R. J. Angelici.

The space group, determined from Weissenberg and precession photographs, was found to be $I4_1/a$. The observed density is approximately 1.5 ± 0.1 g/cm^3, determined by flotation techniques; the calculated density is 1.45 g/cm^3, assuming one molecule per asymmetric unit, 16 molecules per unit cell. The lattice parameters, determined by precession techniques, were found to be $a=b=19.91\pm0.05$ Å, $c=11.90\pm0.05$ Å, with standard deviations estimated from repeated film measurements.

Complete three dimensional x-ray diffraction intenstiy data were taken at room temperature with zirconium-filtered molybdenum K_α radiation from a crystal approximately 0.2 mm in average diameter. A General Electric RD-5 x-ray unit equipped with a single-crystal orienter and scintillation counter was used to collect the data by the stationary-crystal, stationary-counter technique.[2] At a takeoff angle of 8°, a 40-sec peak height intensity was recorded for each of 1753 non-equivalent reflections (including all systematically extinct reflections) in the molybdenum radiation sphere of radius $\sin\Theta/\lambda=0.5385$ ($2\Theta=45°$).

A table of backgroupn intensities, measured at various extinct reflection positions, was prepared and found to be independent of χ and Φ. Various reflections of the $h0l$ type were measured periodically to correct for decomposition effects. The maximum decrease in intensity was 20%. Streak corrections were made using the technique of Benson,[3] a modification of the method of Williams and Rundle.[4] All intensities were corrected for background, streak, decomposition, and Lorentz-polarization effects. Because of the small absorption coefficient ($\mu/\rho=9.0$ cm^2/g), no absorption correction was made. Of the 1753 reflections measured, 1315 were detectable above the background ($|F_o|>0.8$) and were used in the refinement. Errors in intensities were estimated and weights assigned using the method described by Hoard and Jacobson.[5]

Structure Determination. All the atoms are located in general positions in the centrosymmetric space group $I4_1/a$.[6] The positional parameters for the manganese atom were determined from a three-dimensional Patterson map. The rest of the molecular configuration

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(*) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(1) R. J. Angelici, *Chem. Commun.*, *20*, 486 (1965).

(2) T. C. Furnas, «Single Crystal Orienter Instruction Manual», General Electrical Company, Milwaukee, Wisconsin (1957).

(3) J. E. Benson, Iowa State University, Ames, Iowa, private communication.

(4) D. E. Williams and R. E. Rundle, *J. Am. Chem. Soc.*, *86*, 1660 (1964).

(5) L. G. Hoard and R. A. Jacobson, *J. Chem. Soc.*, (A), 1203 (1966).

(6) «International Tables for X-ray Crystallography», Vol. I. The Kynoch Press, Birmingham, England, p. 178 (1952).

was revealed by successive electron-density maps. A difference synthesis was then computed, and it was verified that all non-hydrogen atoms had been located.

A full matrix least-squares refinement was initiated with all atoms isotropic, using the program of Busing *et al.*[7] and the Hartree-Fock-Slater atomic scattering factors.[8] When the reliability index ($R=\Sigma||F_o|-|F_c|/\Sigma|F_o|$) reached 0.151, anisotropic refinement was begun. Then final R-factor was 0.095; the weighted R-factor ($R_{\text{weighted}} = (\Sigma\omega(F_o-F_c)^2/\Sigma\omega F_o^2)^{1/2}$) was 0.083. The observed and calculated structure factors are given in Table I. The final positional parameters,

Table I. Observed and Calculated Structure Factors (the first column contains the running index k, the second $10|F_o|$, and third $10F_c$).

H= 2 , L= 0		
K		
0	631	-526
2	2067	2082
4	519	524
6	117	137
8	513	543
10	229	243
12	186	193
14	353	-351
16	55	8
18	33	-43
20	107	-101
H= 4 , L= 0		
K		
0	821	759
2	211	119
4	54	-10
6	728	736
8	165	-193
10	491	499
12	104	-113
14	347	323
16	71	-53
18	86	-96
H= 6 , L= 0		
K		
0	263	-260
2	719	662
4	310	342
6	556	-531
8	465	490
10	369	-370
12	433	417
14	93	-103
16	121	130
18	46	45
H= 8 , L= 0		
K		
0	309	318
2	528	-539
4	34	52
6	778	749
8	153	-177
10	429	414
14	338	353
16	24	59
H=10 , L= 0		
K		
0	76	-18
2	215	-206
4	235	230
6	79	-61
8	504	517
12	329	343
14	181	177
16	38	-59
18	128	119
H=12 , L= 0		
K		
0	270	-292
4	528	-528
6	152	127
8	309	-307
10	193	159
12	103	101
16	178	172
H=14 , L= 0		
K		
0	262	-253
2	389	-375
6	434	-426
8	152	-181
10	123	-129
14	172	152
H=16 , L= 0		
K		
0	316	-296
2	103	-111
4	346	-340
6	230	-218
8	219	-210
10	140	-145
12	49	57
14	98	-96
H=18 , L= 0		
K		
0	97	94
2	221	-221
6	148	-146
8	149	-146
10	113	-88
H=20 , L= 0		
K		
0	55	-77
2	89	78
H= 0 , L= 1		
K		
1	645	-534
3	399	-405
5	764	-656
7	137	-97
9	700	-715
11	311	-276
13	243	-249
15	380	-375
17	183	-176
19	68	59
H= 1 , L= 1		
K		
2	593	-719
4	736	714
6	319	298
8	76	106
10	259	-254
12	25	-6
14	28	63
16	163	-185
18	225	205
20	139	-94
H= 2 , L= 1		
K		
1	623	541
3	213	123
5	65	84
7	348	-338
9	276	-271
11	554	-545
13	265	-243
15	190	-212
17	165	-159
19	102	-121
H= 3 , L= 1		
K		
2	278	321
4	861	-797
6	505	473
8	50	-102
10	177	192
12	98	-109
14	109	-107
16	185	190
18	196	-190
20	133	119
H= 4 , L= 1		
K		
1	734	669
3	224	-292
5	469	451
7	137	-149
9	212	-201
11	63	-55
13	218	-216
15	388	-406
17	258	-259
19	73	-89
H= 5 , L= 1		
K		
2	322	-353
4	132	114
6	655	-638
8	50	-15
10	61	-91
12	57	-58
14	262	254
16	198	-211
18	111	108
20	108	-85
H= 6 , L= 1		
K		
1	290	-259
3	733	749
5	114	-100
7	53	57
9	37	38
13	239	-249
15	82	-80
17	127	-140
19	51	-41
H= 7 , L= 1		
K		
2	323	332
4	386	-392
6	212	225
8	286	266
10	221	-225
12	175	192
14	260	-273
16	161	168
18	106	-110
20	105	103
H= 8 , L= 1		
K		
1	185	189
3	517	524
5	805	786
7	195	211
9	91	-38
11	38	22
13	39	82
15	77	-90
19	16	-76
H= 9 , L= 1		
K		
2	32	18
4	498	506
6	116	125
8	59	-82
10	238	219
12	163	-177
14	277	267
16	129	-127
18	96	69
H=10 , L= 1		
K		
1	155	166
3	483	455
5	293	298
7	428	432
9	289	293
11	96	103
13	40	42
17	36	-69
H=11 , L= 1		
K		
2	361	371
4	61	8
6	155	147
8	50	-54
10	111	-88
12	278	282
14	51	-66
H=12 , L= 1		
K		
3	38	-15
5	555	549
7	383	378
9	327	315
11	337	250
13	83	88
17	49	34
H=13 , L= 1		
K		
2	376	-372
4	96	82
8	99	-80
10	77	59
12	114	-107
14	59	66
H=14 , L= 1		
K		
5	133	140
7	253	254
9	219	237
11	119	133
13	88	90
15	89	74
H=15 , L= 1		
K		
2	88	100
4	33	-50
6	76	-55
10	147	-155
14	108	-86
H=16 , L= 1		
K		
1	175	-180
3	72	-63
5	52	-71
9	134	131
11	139	128
13	33	34
H=17 , L= 1		
K		
2	56	-66
4	77	-102
6	56	61
8	46	-106
10	81	87
12	90	-75
H=18 , L= 1		
K		
1	186	-173
3	178	-167
5	106	-109
7	26	17
9	85	60
11	51	55
H=19 , L= 1		
K		
4	174	156
6	88	-65
8	87	77
H=20 , L= 1		
K		
1	134	-108
3	89	-76
5	82	-55
H=21 , L= 1		
K		
2	106	94
4	54	-45
H= 0 , L= 2		
K		
2	1415	-1299
4	292	261
6	323	-313
8	105	-120
10	338	348
12	138	-146
14	437	440
16	82	64
18	232	237
20	118	85
H= 1 , L= 2		
K		
1	71	-71
3	15	62
7	277	282
9	80	74
13	56	50
15	113	-135
17	52	61
21	58	24
H= 2 , L= 2		
K		
2	214	-175
4	348	-419
6	71	-110
8	100	118
10	541	-546
12	167	170
14	215	-201
16	143	139
20	39	19
H= 3 , L= 2		
K		
1	294	306
3	706	625
5	1484	1485
7	31	107
9	15	57
15	49	-68
H= 4 , L= 2		
K		
2	933	-925
4	805	-764
6	508	-499
8	823	-830
10	100	-123
12	513	-510
16	93	-94
20	71	63
H= 5 , L= 2		
K		
1	499	-509
3	185	164
5	614	584
7	224	252
11	195	189
15	125	-143
19	29	42
H= 6 , L= 2		
K		
2	573	-539
4	497	-489
6	490	-510
10	678	-683
12	55	-57
14	258	-243
16	80	-78
H= 7 , L= 2		
K		
1	139	-83
5	211	-201
7	262	254
9	44	-19
11	18	48
13	101	-113
15	20	38
19	61	-3
H= 8 , L= 2		
K		
4	199	-220
8	562	-567
10	93	64
12	408	-418
14	129	-117
18	39	-126
H= 9 , L= 2		
K		
3	91	126
7	85	-50
9	146	60
13	84	-54
15	139	-148
17	39	-70
H=10 , L= 2		
K		
4	290	279
6	213	-208
8	222	226
10	399	-420
16	118	-144
H=11 , L= 2		
K		
3	54	-43
5	144	152
7	61	54
9	144	148
11	111	-74
15	79	-115
H=12 , L= 2		
K		
2	476	467
6	400	393
10	112	130
12	22	-43
14	148	-169
16	67	23
H=13 , L= 2		
K		
3	174	176
5	54	58
9	46	-59
11	143	165
15	19	49
H=14 , L= 2		
K		
4	438	429
6	47	75
8	134	146
12	85	-88
14	28	24
H=15 , L= 2		
K		
5	84	93
11	32	60
H=16 , L= 2		
K		
2	363	352
6	240	230
8	122	134
10	49	90
12	91	61
H=17 , L= 2		
K		
1	140	-144
3	17	-61
7	81	105
9	83	88
11	86	-69
H=18 , L= 2		
K		
4	218	223
6	123	114
8	124	134
10	131	117
H=19 , L= 2		
K		
3	24	29
7	52	12
9	48	-38
H=20 , L= 2		
K		
2	171	146
6	125	92
H= 0 , L= 3		
K		
1	258	-204
3	376	330
5	211	-230
7	745	695
9	288	282
11	192	178
13	273	285
15	168	170
19	46	62
H= 1 , L= 3		
K		
0	262	-204
2	55	57
4	681	672
6	824	-815
8	493	502
12	19	53
14	130	130
16	29	3
18	89	69
20	144	-130
H= 2 , L= 3		
K		
1	250	-244
3	196	-239
5	728	705
7	208	205
9	158	-161
11	107	131
13	233	235
15	108	121
17	219	223
H= 3 , L= 3		
K		
2	116	150
4	788	-777
6	401	385
8	418	-431
10	65	-58
12	83	82
14	147	-142
16	80	55
18	168	-168
20	65	56
H= 4 , L= 3		
K		
1	301	-313
3	897	-877
5	69	-70
7	81	77
9	451	450
11	158	142
13	241	245
15	195	198
19	129	106
H= 5 , L= 3		
K		
0	218	-230
2	892	-858
4	914	867
6	423	-409
8	185	191
10	146	-154
12	315	-320
14	112	119
16	111	-121
18	184	165
20	64	-100
H= 6 , L= 3		
K		
1	1060	-1075
5	346	-368
7	115	-113
9	151	-130
11	333	342
15	40	49
17	94	109
19	148	138
H= 7 , L= 3		
K		
0	732	-695
2	319	318
4	391	-370
6	575	575
8	223	-222
10	29	-30
12	235	237
14	132	-148
16	159	178
18	83	-93
H= 8 , L= 3		
K		
1	384	-376
3	517	-503
5	190	-213
7	412	-412
9	214	-203
11	286	-283
13	82	81
17	119	101
19	106	83
H= 9 , L= 3		
K		
2	263	-280
4	96	116
6	205	-222
8	99	102
10	209	202
12	241	-246
14	159	156
18	27	40
H=10 , L= 3		
K		
1	368	-377
3	79	-114
5	366	-372
7	255	-258
9	199	-213
13	107	-94
H=11 , L= 3		
K		
0	169	-178
2	121	125
4	128	-148
6	130	133
8	275	275
10	236	-229
12	40	54
14	212	-196
16	66	75
H=12 , L= 3		
K		
1	61	77
3	235	-236
5	50	-47
7	166	-153
9	154	-142
11	180	-155
13	76	-121
15	53	-61
17	140	-99
H=13 , L= 3		
K		
0	292	285
2	143	-129
6	38	-61
8	157	-150
10	87	99
12	170	-174
14	97	80
16	85	-93
H=14 , L= 3		
K		
5	70	-100
7	206	-220
9	156	-161
11	12	-88
13	102	-90
15	155	-124
H=15 , L= 3		
K		
4	36	-50
6	149	-153
10	106	-119
12	60	91
14	76	-62
H=16 , L= 3		
K		
1	68	89
11	100	-97
13	150	-145
H=17 , L= 3		
K		
0	73	-54
4	41	-53
6	114	135
8	93	-79
10	130	111
H=18 , L= 3		
K		
3	43	83
5	54	27
7	33	-31
9	58	-55
H=19 , L= 3		
K		
0	101	-62
4	59	89
6	94	-66
8	96	109
H=20 , L= 3		
K		
1	147	146
3	86	100
5	71	60
H= 0 , L= 4		
K		
0	527	-507
2	145	120
4	891	900
6	538	554
8	47	-88
10	445	453
12	300	-303
14	110	102
16	270	-275
H= 1 , L= 4		
K		
1	683	672
3	215	-230
5	344	311
7	379	358
9	99	-132
11	140	143
13	72	91
19	52	-29
H= 2 , L= 4		
K		
0	171	-120
2	501	539
4	390	389
6	78	-44
8	526	559
10	272	-276
12	360	373
14	195	-197
16	113	108
18	66	-105
20	145	-143
H= 3 , L= 4		
K		
1	41	98
3	335	349
7	215	-214
9	197	211
11	38	17
19	50	4
H= 4 , L= 4		
K		
2	46	24
4	250	279
6	569	554
10	460	470
14	166	164
16	116	-106
18	75	-59
H= 5 , L= 4		
K		
1	152	-164
3	135	-152
5	145	-128
9	155	-148
11	10	21
13	118	138
19	54	-15
H= 6 , L= 4		
K		
0	575	-554
2	196	200
4	425	436
6	230	242
8	591	637
10	243	258
12	260	272
14	31	76
18	130	112
H= 7 , L= 4		
K		
3	97	-78
5	234	-246
7	155	-157
9	197	-209
11	43	-51
17	76	28
19	40	21
H= 8 , L= 4		
K		
2	19	48
4	159	-189
6	365	368
8	60	53
10	623	627
12	276	285
14	199	223
16	213	220
18	48	13
H= 9 , L= 4		
K		
1	216	-240
3	230	-256
5	73	-14
7	356	-377
9	73	-60
11	14	13
13	89	67
17	58	49
H=10 , L= 4		
K		
0	476	-453
2	99	87
4	371	373
6	327	-340
8	403	406
10	40	42
12	136	136
14	101	124
16	174	165
H=11 , L= 4		
K		
3	92	79
5	134	-120
7	24	19
9	14	-6
H=12 , L= 4		
K		
2	182	-210
4	406	-408
6	178	198
8	196	-204
10	32	38
12	28	78
14	122	114
16	120	125
H=13 , L= 4		
K		
3	11	35
5	37	-59
9	50	-78
13	54	-36
15	29	-41
H=14 , L= 4		
K		
0	96	-102
2	443	-448
4	111	-94
6	375	-370
8	47	60
10	23	8
14	118	80
H=15 , L= 4		
K		
1	113	99
3	31	-40
7	57	-111
11	46	9
13	84	6
H=16 , L= 4		
K		
2	47	-45
4	299	-290
6	68	81
8	159	-151
10	129	-114
12	33	-42
H=17 , L= 4		
K		
7	111	-99
9	36	16
H=18 , L= 4		
K		
2	152	-166
6	255	-239
8	13	-67
H=19 , L= 4		
K		
5	63	-62
H=20 , L= 4		
K		
2	64	43
H= 0 , L= 5		
K		
1	100	-104
3	98	-73
5	408	-413
7	576	-569
9	212	-214
11	227	-237
15	65	-29
19	78	-34
H= 1 , L= 5		
K		
0	91	104
2	175	161
4	463	457
6	541	-566
8	464	475
10	151	-159
12	128	134
16	58	-93
18	132	146
H= 2 , L= 5		
K		
1	81	113
3	96	63
5	132	-140
9	276	-285
11	87	42
13	198	-210
15	67	-73
17	52	-44
19	87	-84
H= 3 , L= 5		
K		
0	83	-73
2	499	532
4	395	-394
6	208	224
8	256	-244
10	243	259
14	122	-115
18	162	-160
H= 4 , L= 5		
K		
1	160	153
3	396	414
5	90	96
7	175	-178
9	81	-80
11	266	-276
13	129	-141
17	99	-107
19	42	-69
H= 5 , L= 5		
K		
2	350	-350
4	605	613
6	253	-248
8	183	181
10	63	26
12	38	-71
14	91	-81
16	201	-219
18	102	99
H= 6 , L= 5		
K		
1	726	731
3	201	226
5	47	43
7	68	96
9	168	-171
11	109	-139
17	125	-111
H= 7 , L= 5		
K		
0	574	-569
2	521	523
4	422	-431
6	68	61
8	169	-165
10	89	107
12	177	168
16	89	106
18	86	-74
H= 8 , L= 5		
K		
1	171	201
3	104	95
5	388	423
7	188	178
9	266	282
11	170	161
13	40	42
15	90	-108
17	79	-87
H= 9 , L= 5		
K		
0	210	214
2	390	-399
4	215	222
6	173	-188
10	215	232
12	29	67
14	142	167
16	28	-5
H=10 , L= 5		
K		
1	507	491
3	428	451
5	146	156
7	276	295
9	129	135
11	127	126
13	52	73
15	114	125
H=11 , L= 5		
K		
0	228	-237
2	270	270
4	128	-113
6	32	-57
8	198	233
10	127	-131
14	108	-68
16	124	116
H=12 , L= 5		
K		
1	218	238
3	344	347
5	258	278
7	91	91
9	80	121
11	183	198
13	131	142
15	101	119
H=13 , L= 5		
K		
0	45	25
6	89	50
8	169	-179
10	198	202
12	76	-93
14	81	101
H=14 , L= 5		
K		
1	41	48
7	143	145
9	145	139
11	56	68
13	193	183
H=15 , L= 5		
K		
6	33	-79
8	170	170
10	144	-154
12	63	71
H=16 , L= 5		
K		
1	64	-98
7	65	-52
9	68	-26
11	106	100
H=17 , L= 5		
K		
2	30	-53
6	33	49
8	153	-152
10	44	74
H=18 , L= 5		
K		
1	104	-96
3	76	-79
5	132	-107
7	80	-7
H=19 , L= 5		
K		
0	90	-34
2	67	-38
4	62	-62
H= 0 , L= 6		
K		
0	56	0
2	456	-450
4	92	-112
6	322	-335
8	461	-455
10	294	287
12	144	-140
14	298	303
18	146	140
H= 1 , L= 6		
K		
1	63	76
3	53	72
5	178	-179
7	175	-165
9	186	-187
11	70	100
13	55	75
H= 2 , L= 6		
K		
0	411	-450
2	133	-147
4	573	-600
6	456	-476
8	65	-19
10	457	-470
12	228	238
14	148	-157
18	60	58
H= 3 , L= 6		
K		
1	65	42
3	189	-187
5	79	-115
9	151	162
15	46	55
H= 4 , L= 6		
K		
0	90	112
2	312	-326
4	258	-257
6	288	-304
8	636	-667
10	116	133
12	375	-390
H= 5 , L= 6		
K		
1	139	127
3	368	365
5	410	-419
7	19	-53
9	70	-99
11	204	-212
H= 6 , L= 6		
K		
2	97	135
4	41	-4
6	401	-415
12	58	-38
14	99	-150
16	147	-142
H= 7 , L= 6		
K		
1	262	270
3	186	-197
5	271	273
9	57	-97
13	49	-55
17	134	-125
H= 8 , L= 6		
K		
0	430	455
2	150	147
4	146	-189
8	324	-335
12	232	-225
14	181	-175
16	52	-39
H= 9 , L= 6		
K		
1	122	-121
3	91	58
7	50	-54
9	77	112
11	50	-7
H=10 , L= 6		
K		
0	262	287
2	32	45
4	238	255
6	243	-231
8	62	69
10	201	-195
14	161	-161
16	187	-182
H=11 , L= 6		
K		
1	47	85
7	38	46
9	156	-157
11	46	60
13	56	86
15	130	127
H=12 , L= 6		
K		
2	360	371
4	27	-76
6	166	177
8	155	-168
12	183	-184
14	157	-131
H=13 , L= 6		
K		
1	68	-78
5	8	-19
9	188	192
11	84	-10
13	44	56
H=14 , L= 6		
K		
0	273	303
4	204	200
6	107	-119
8	130	142
10	94	-81
12	46	-5
H=15 , L= 6		
K		
7	78	92
9	98	-106
11	62	5
H=16 , L= 6		
K		
2	196	218
6	163	164
8	53	26
10	72	97
H=17 , L= 6		
K		
3	59	26
7	102	-95
H=18 , L= 6		
K		
4	167	177
H= 0 , L= 7		
K		
1	131	153
3	256	269
5	213	197
7	383	340
9	486	489
11	157	132
13	250	261
17	200	173
H= 1 , L= 7		
K		
0	149	153
2	132	-122
4	263	275
6	268	-276
8	307	300
10	218	-213
12	29	36
14	113	129
16	117	-129
H= 2 , L= 7		
K		
3	137	135
5	76	37
7	166	148
9	287	280
11	456	454
13	39	46
15	136	149
17	86	66
H= 3 , L= 7		
K		
0	258	-269
2	109	86
4	227	-245
6	229	224
8	512	-512
10	79	-8
12	29	9
14	159	-180
16	166	157
H= 4 , L= 7		
K		
1	213	-236
3	142	-136
5	195	-201
9	80	84
11	65	49
13	150	135
15	82	90
17	103	75
H= 5 , L= 7		
K		
0	200	197
2	404	-406
4	187	-200
6	510	-523
10	144	-140
12	86	-97
14	185	193
16	95	-92
H= 6 , L= 7		
K		
1	193	-183
3	348	-369
5	190	-187
7	199	-219
9	115	-115
11	141	-141
15	81	65
H= 7 , L= 7		
K		
2	242	238
4	234	-238
10	29	-65
12	61	9
14	206	-207
16	76	51
H= 8 , L= 7		
K		
1	393	-390
3	377	-398
5	304	-315
7	23	-66
9	77	-79
H= 9 , L= 7		
K		
0	469	489
2	208	-218
4	204	215
12	124	-164
14	101	72
H=10 , L= 7		
K		
1	258	-270
3	214	-215
5	197	-211
7	102	-117
9	131	-131
H=11 , L= 7		
K		
0	143	-132
2	281	281
4	43	31
12	149	144
14	142	-120
H=12 , L= 7		
K		
1	8	-41
3	191	-171
5	81	-67
7	61	-123
11	166	-130
13	144	-133
H=13 , L= 7		
K		
0	249	261
2	58	81
4	9	50
6	94	114
10	112	110
12	156	-142
H=14 , L= 7		
5	112	-134
9	89	-85
11	182	-177
H=15 , L= 7		
K		
0	50	-17
2	103	88
4	104	95
8	100	114
H=16 , L= 7		
K		
1	92	108
7	37	-45
H=17 , L= 7		
K		
0	178	173
2	99	52
4	37	4
H= 0 , L= 8		
K		
0	794	803
2	72	55
4	317	323
6	76	43
8	135	116
10	144	58
12	217	-219
14	177	192
16	127	-150
H= 1 , L= 8		
K		
1	79	-14
3	197	194
7	290	282
9	164	151
11	55	46
H= 2 , L= 8		
K		
0	94	-55
2	446	437
4	210	225
6	469	500
8	331	330
12	233	233
14	192	-187
16	94	54
H= 3 , L= 8		
K		
1	85	1
3	118	-120
5	192	202
7	101	96
9	178	182
13	85	-80
15	74	87
H= 4 , L= 8		
K		
0	304	323
2	95	110
4	282	295
6	332	349
8	114	108
10	382	373
12	60	-102
14	190	177
H= 5 , L= 8		
K		
1	98	-133
5	154	-160
7	79	92
9	99	56
11	33	17
13	77	80
15	98	-46
H= 6 , L= 8		
K		
0	90	-43
2	148	159
4	247	280
6	8	-65
8	308	297
12	241	254
14	53	-10
H= 7 , L= 8		
K		
3	155	-152
7	79	-59
11	41	30
13	149	-146
15	62	45
H= 8 , L= 8		
K		
2	121	117
4	99	-95
6	371	367
10	110	119
14	150	134
H= 9 , L= 8		
K		
1	220	-224
3	113	-104
5	86	-108
7	87	119
13	91	87
H=10 , L= 8		
K		
0	127	-58
2	285	-291
4	126	142
6	23	-93
8	115	116
12	219	205
H=11 , L= 8		
K		
1	117	133
3	77	47
H=12 , L= 8		
K		
0	224	-219
4	215	-244
6	13	85
8	50	-82
10	121	116
H=13 , L= 8		
K		
7	44	-74
9	23	11
H=14 , L= 8		
K		
0	196	-192
2	227	-231
6	203	-204
H=15 , L= 8		
K		
1	21	9
3	36	23
5	119	-108
H=16 , L= 8		
K		
2	57	-47
4	258	-255
H= 0 , L= 9		
K		
1	252	-271
3	116	-90
5	155	-129
7	209	-198
9	132	-95
11	267	-254
13	38	-32
15	163	-159
H= 1 , L= 9		
K		
0	276	271
2	117	-85
4	371	360
6	78	-50
8	198	181
10	76	-90
12	81	-13
14	77	70
H= 2 , L= 9		
K		
1	387	390
3	110	88
7	91	19
9	214	-217
11	112	-130
13	203	-188
15	26	-13
H= 3 , L= 9		
K		
0	95	-90
2	254	253
4	124	-109
6	383	376
8	58	59
14	111	-90
H= 4 , L= 9		
K		
1	67	53
3	76	67
5	156	161
11	106	-93
13	72	-48
H= 5 , L= 9		
K		
0	153	129
2	224	-199
4	297	290
6	82	-32
12	75	-59
14	197	162
H= 6 , L= 9		
K		
1	219	217
3	166	153
5	97	114
7	118	113
11	38	-16
13	223	-191
H= 7 , L= 9		
K		
0	225	-198
2	195	212
4	187	-198
6	133	102
10	26	-81
12	85	45
H= 8 , L= 9		
K		
1	170	162
3	215	224
5	95	96
9	93	53
11	79	-90
13	48	-72
H= 9 , L= 9		
K		
2	265	-287
4	163	189
8	58	45
10	127	106
H=10 , L= 9		
K		
1	82	99
3	124	131
5	53	57
7	156	160
9	64	77
11	151	127
H=11 , L= 9		
K		
0	278	-254
2	93	120
4	128	-142
6	51	43
8	55	50
H=12 , L= 9		
K		
1	50	91
5	213	214
7	113	123
9	199	199
H=13 , L= 9		
K		
0	84	32
2	251	-249
4	72	60
6	48	-19
8	84	-95
H=14 , L= 9		
1	77	-64
K		
3	147	132
H=15 , L= 9		
K		
0	171	-159
H= 0 , L=10		
K		
2	449	-463
4	75	6
6	196	-210
8	60	-2
10	79	105
12	175	-163
H= 1 , L=10		
K		
1	97	-48
3	138	120
5	150	-131
7	74	-90
9	66	-66
13	59	-75
H= 2 , L=10		
K		
0	485	-463
2	42	-3
4	366	-376
6	162	-145
8	95	-89
10	215	-228
12	143	115
H= 3 , L=10		
K		
1	259	261
3	44	32
5	121	149
7	28	30
9	114	-92
11	76	-70
13	82	-20
H= 4 , L=10		
K		
2	412	-397
4	167	-159
6	117	-129
8	239	-249
10	76	50
12	172	-187
H= 5 , L=10		
K		
1	101	-89
3	44	75
11	73	23
H= 6 , L=10		
K		
0	220	-210
2	156	-148
4	140	-134
6	273	-273
10	260	-252
12	69	49
H= 7 , L=10		
K		
1	111	96
9	60	-63
H= 8 , L=10		
K		
6	121	119
8	228	-208
10	17	-10
H= 9 , L=10		
K		
1	60	23
3	214	215
5	58	22
7	69	50
9	34	59
H=10 , L=10		
K		
2	69	61
4	168	169
6	71	-55
8	91	89
H=11 , L=10		
K		
1	149	148
5	137	139
7	140	147
H=12 , L=10		
K		
0	190	163
2	147	150
4	32	16
6	149	159
H=13 , L=10		
K		
3	107	103
H= 0 , L=11		
K		
1	140	-149
3	90	87
5	120	98
7	110	60
9	147	143
11	142	139
H= 1 , L=11		
K		
0	171	-149
2	184	-183
4	41	-29
6	224	-212
8	197	194
10	57	-37
H= 2 , L=11		
K		
1	173	177
3	116	98
5	131	123
7	224	223
9	84	47
H= 3 , L=11		
K		
0	64	-87
2	61	39
4	218	-197
6	88	78
8	118	-102
10	27	28
H= 4 , L=11		
K		
1	93	-90
3	20	19
5	86	111
9	148	128
H= 5 , L=11		
K		
0	49	98
2	163	-149
4	92	64
6	130	-114
8	83	46
H= 6 , L=11		
K		
1	169	-167
3	131	-132
5	211	-211
7	39	-27
9	143	-123
H= 7 , L=11		
K		
0	89	-60
2	105	91
4	81	-118
8	133	-142
H= 8 , L=11		
K		
1	218	-190
3	174	-157
5	90	-64
7	271	-256
H= 9 , L=11		
K		
0	175	143
2	113	-100
4	63	-1
6	151	-147
H=10 , L=11		
K		
1	82	-92
3	101	-61
H= 0 , L=12		
K		
2	103	-56
4	252	239
6	55	50
H= 1 , L=12		
K		
1	106	-20
3	100	104
5	124	-115
7	92	86
H= 2 , L=12		
K		
0	143	56
2	336	323
4	112	63
6	51	53
H= 3 , L=12		
K		
1	89	-46
3	118	-87
5	124	91
H= 4 , L=12		
K		
0	279	239
2	112	61
4	179	165
6	179	193
H= 5 , L=12		
K		
1	182	-148
3	65	-55
5	104	-94
H= 6 , L=12		
K		
0	111	-50
2	91	67
4	93	97
H= 7 , L=12		
K		
1	119	-118

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[7] W. R. Busing, K. O. Martin, and H. A. Levy, «OR FLS, a Fortran Crystallographic Least-Squares Program», ORNL-TM-305, (1962).

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

anisotropic temperature factors, and standard errors are given in Tables IIa and IIb. The more important interatomic distances and angles, and their errors, were calculated using the function and error program of Busing *et al.*[9] and are summarized in Table III.

Table IIa. Final Atomic Parameters (The origin is at $\bar{1}$. Standard errors ×10⁴ are given in parentheses after the parameters)

Atom	x	y	z
Mn	0.2738(1)	0.7878(1)	0.5069(1)
C(1)	0.3403(6)	0.7458(5)	0.5907(8)
O(1)	0.3834(4)	0.7244(4)	0.6401(7)
C(2)	0.3393(6)	0.8244(5)	0.4264(9)
O(2)	0.3815(4)	0.8454(4)	0.3706(7)
C(3)	0.2142(6)	0.8457(6)	0.4394(8)
O(3)	0.1810(5)	0.8857(5)	0.3977(7)
C(4)	0.2668(6)	0.7219(5)	0.3986(8)
O(4)	0.2643(5)	0.6844(4)	0.3268(6)
N(1)	0.1980(4)	0.7425(4)	0.6051(6)
C(5)	0.1372(6)	0.7130(6)	0.5523(10)
C(6)	0.2752(5)	0.8590(5)	0.6340(8)
O(5)	0.2431(3)	0.8503(3)	0.7232(5)
N(2)	0.3123(4)	0.9152(4)	0.6255(6)
C(7)	0.3138(5)	0.9666(5)	0.7142(8)

Table IIb. Final Anisotropic Temperature Coefficients ×10⁵ (Standard errors ×10⁵ are given in parentheses after the parameter) [a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	305(5)	239(4)	418(9)	23(4)	56(7)	16(6)
C(1)	289(37)	245(33)	739(86)	4(27)	172(46)	48(45)
O(1)	344(27)	475(32)	1404(90)	107(23)	−85(42)	211(42)
C(2)	437(45)	314(38)	619(86)	31(32)	66(51)	−26(46)
O(2)	550(34)	493(32)	1047(75)	−109(25)	317(42)	36(41)
C(3)	436(43)	399(42)	334(70)	5(34)	12(47)	−31(46)
O(3)	590(37)	551(35)	1015(81)	251(30)	−118(43)	139(44)
C(4)	504(44)	318(38)	469(73)	26(33)	11(48)	71(47)
O(4)	985(52)	408(32)	704(65)	−11(32)	−14(47)	−220(37)
N(1)	253(26)	299(27)	706(63)	−38(20)	12(34)	−9(35)
C(5)	323(37)	407(41)	1368(123)	−108(32)	−86(57)	−142(60)
C(6)	252(30)	281(32)	491(75)	34(25)	70(40)	−46(41)
O(5)	308(21)	304(21)	614(56)	−27(16)	107(28)	−69(27)
N(2)	334(28)	277(26)	598(62)	−41(22)	29(35)	−41(35)
C(7)	428(40)	334(35)	675(88)	−143(31)	0(45)	−64(44)

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

Table III. Selected Interatomic Distances and Angles in $(Mn(CO)_4(NH_2CH_3)(CONHCH_3)$ [a]

Atoms	Distances (Å)	Atoms	Angle, deg.
Mn–C(1)	1.856 (0.012)	Mn–C(1)–O(1)	174.9 (1.0)
Mn–C(2)	1.775 (0.013)	Mn–C(2)–O(2)	176.5 (1.0)
Mn–C(3)	1.839 (0.013)	Mn–C(3)–O(3)	174.4 (1.1)
Mn–C(4)	1.845 (0.012)	Mn–C(4)–O(4)	175.2 (0.9)
Mn–N(1)	2.111 (0.008)	Mn–N(1)–C(5)	121.1 (0.7)
Mn–C(6)	2.072 (0.011)	Mn–C(6)–O(5)	121.2 (0.7)
C(1)–O(1)	1.124 (0.011)	Mn–C(6)–N(2)	121.4 (0.7)
C(2)–O(2)	1.148 (0.011)	C(1)–Mn–C(3)	167.8 (0.4)
C(3)–O(3)	1.146 (0.011)	C(2)–Mn–N(1)	178.3 (0.4)
C(4)–O(4)	1.135 (0.011)	C(4)–Mn–C(6)	175.7 (0.4)
N(1)–C(5)	1.484 (0.012)	C(1)–Mn–C(2)	87.2 (0.5)
C(6)–O(5)	1.251 (0.010)	C(1)–Mn–C(4)	96.2 (0.5)
C(6)–N(2)	1.345 (0.012)	C(1)–Mn–N(1)	91.1 (0.4)
N(2)–C(7)	1.470 (0.012)	C(1)–Mn–C(6)	84.7 (0.4)
		C(2)–Mn–C(3)	88.9 (0.5)
		C(2)–Mn–C(4)	88.3 (0.5)
		C(2)–Mn–C(6)	96.0 (0.5)
		C(3)–Mn–C(4)	95.2 (0.5)
		C(3)–Mn–N(1)	92.8 (0.4)
		C(3)–Mn–C(6)	84.2 (0.4)
		C(4)–Mn–N(1)	91.6 (1.4)
		N(1)–Mn–C(6)	84.1 (0.4)
		O(5)–C(6)–N(2)	117.4 (0.8)
		C(6)–N(2)–C(7)	122.4 (0.8)

[a] The number in parenthesis after the distance or angle is the standard deviation.

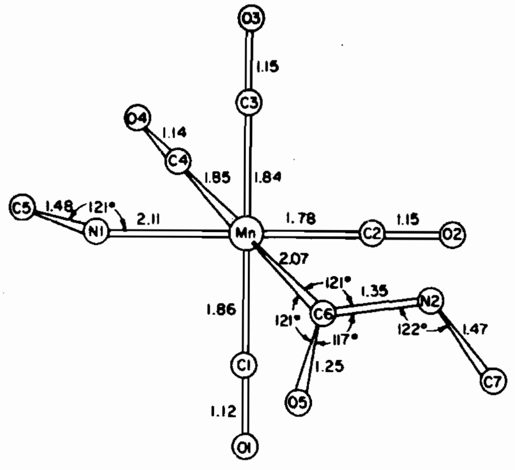

Figure 1. Molecular structure of $Mn(CO)_4(NH_2CH_3)(CONHCH_3)$.

Results and Discussion

Each manganese atom is surrounded by four carbonyl groups, one methyl amine, and one N-methylcarboxamido group in approximately octahedral configuration (see Figure 1). The average manganese-carbonyl bond distance, excluding the carbonyl group opposite the NH_2CH_3 group, is 1.847±0.010 Å, in reasonably good agreement with 1.825 and 1.83 Å found for π-$C_5H_5Fe(CO)_2Mn(CO)_5$[10] and $Mn_2(CO)_{10}$,[11] respectively. The remaining manganese-carbonyl distance of 1.775±0.013 Å appears to be significantly shorter than the other three. Indeed, some shortening would be expected due to the *trans* effect of the NH_2CH_3 group. A similar shortening of some of the manganese-carbon distances can also be seen in π-$C_5H_5Fe(CO)_2Mn(CO)_5$ (1.749Å),[10] $Mn_2(CO)_{10}$ (1.79Å),[11] and in $(BrMn(CO)_4)_2$ (1.78Å).[12] In the last two cases the effect was less certain due to larger standard deviations. Since the magnitude of the *trans* effect should be somewhat different in each of these cases the *trans* Mn–C distance would be expected to vary slightly. In the present study a distance similar to that found in $(BrMn(CO)_4)_2$ might be expected, as indeed was found. The carbon-oxygen distances in the carbonyls are all approximately normal to within the standard deviations.

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(9) W. R. Busing, K. O. Martin, and H. A. Levy, «OR FFE, a Fortran Crystallographic Function and Error Program», ORNL-TM-306 (1964).

(10) P. J. Hansen and R. A. Jacobson, *J. Organomet.*, *6*, 389 (1966).

(11) L. F. Dahl and R. E. Rundle, *Acta Cryst.*, *16*, 419 (1963).

(12) L. F. Dahl and C. Wei, *Acta Cryst.*, *16*, 611 (1963).

The Mn–N(1)–C(5) bond angle of 121.1° is somewhat larger than the tetrahedral angle. This large angle is presumably caused by the repulsion of the methyl group from C(3) and C(4). The C(3)–C(5) distance is 3.34 Å and the C(4)–C(5) distance is 3.17 Å, both being somewhat less than the sum of the van der Waals radii of the two atoms, approximately 3.6 Å.

The O(5) atom is 2.72 Å away from N(1) in the same molecule. Distances on the order of 2.8 Å are normal for approximately linear hydrogen bonds. However, the Mn–N(1)–O(5) angle is 73.3° and the C(5)–N(1)–O(5) angles is 143.1°, indicating strong hydrogen bonding to be unlikely in this case. The other hydrogen atom on N(1) could possibly form a weak intermolecular hydrogen bond with an O(5) atom on an adjacent molecule. The N(1)–O(5)′ distance is 2.99 Å and the C(5)–N(1)–O(5)′ angles is 111° (see Figure 2). However the Mn–N(1)–O(5) angle is small, also 111°, indicating only very weak, if any, hydrogen bonding.

The C(6)–N(2) distance of 1.35 Å implies about 50% double bond character.[13] In addition the Mn, C(6), O(5), N(2), and C(7) atoms all lie wqithin 0.01 Å of the best least-squares plane containing these atoms. The planarity of this group and the fact that all bond angles are approximately 120°, indicate that C(6) and N(2) are essentially sp^2 hybridized.

The plane containing the N-methylcarboxamido group is tilted about 9° from the plane containing Mn, C(2), O(2), C(4), O(4), N(1), and C(6). This many be explained by intermolecular van der Waals repulsions among C(7) methyl groups. Each C(7) atom is 3.60 Å from two other C(7) atoms on neighboring molecules (the sum of the van der Waals radii is 4.0 Å for two methyl groups). The fact that the C(2)–Mn–C(6) angle is 96° may also be due to van der Waals repulsions between C(2) and N(2) which are 3.03 Å apart. The sum of the van der Waals radii for these two atoms is approximately 3.1 Å.

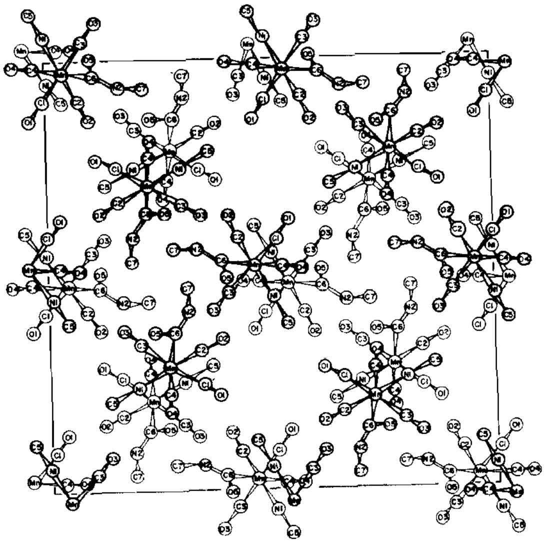

Figure 2. Crystal structure projected down the c axis.

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(13) L. Pauling, «Nature of the Chemical Bond», Cornell University Press, Ithaca, New York, p. 239 (1960).