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The Crystal Structure of the Monoclinic Form of $Mn(CO)_4(NH_2CH_3)(CONHCH_3)$*

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The crystal structure of the monoclinic from of $Mn(CO)_4(NH_2CH_3)(CONHCH_3)$ has been determined using X-Ray diffraction techniques. The space group is $P2_1/n$ with four molecules per unit cell and lattice constants a = 10.79, b = 15.98, c = 6.28 Å, and β = 97.3°. The conventional discrepancy index R = 0.098 for 467 reflections. The molecule is essentially octahedral and virtually identical to that found in the tetragonal form. In both crystalline forms pairs of molecules are held together by two weak hydrogen bonds. The packing of these pairs seems to be unrelated in the two structures. However, the energies of the two forms must be similar as both forms grow simultaneously.

Introduction

A compound of empirical formula $MnC_7H_9O_5N_2$ has recently been prepared^1 and, on the basis of the infrared and nuclear magnetic resonance measurements, has been reported to be seven-coordinated. An X-Ray structure determination of the tetragonal crystals obtained showed this compound to be actually the six-coordinated species $Mn(CO)_4(NH_2CH_3)(CONHCH_3)$.^{2} However, a monoclinic form of a substance with the same empirical formula was also isolated. A structural study of the latter form was undertaken to see if this could be the seven-coordinated species indicated in the spectral measurements.

Experimental Section

Crystals of the compound were kindly supplied by Dr. R. J. Angelici.

The space group was determined to be $P2_1/n$ from Mo Kα precession photographs. The lattice constants were also determined from these photographs and were found to be a = 10.79±.01 Å, b = 15.98±.02 Å, c = 6.28±01 Å, and β = 93.7±.1° with standard deviations estimated from several film measurements. The calculated density for four molecules per unit cell is 1.59 g/cm^3 compared to 1.58 g/cm^3 found by flotation.

Intensity data were measured on a General Electric XRD-5 X-Ray unit equipped with a single crystal orienter and scintillation counter using zirconium-filtered molybdenum Kα radiation. Because of severe decomposition of the crystal in the X-Ray beam, a 40-sec peak height intensity was recorded using the stationary-crystal, stationary-counter technique for 838 non-equivalent reflections. Because of this decomposition, 467 reflections were measured from one crystal and 371 from a second crystal, both approximately 0.1 mm in average diameter.

A table of background intensities was prepared and found to be χ and Φ independent. Three reflections were measured periodically to correct for decomposition effects. The maximum decrease in intensity for the first crystal was 8% for the 467 reflections recorded, after which the crystal suddenly decomposed. For the second crystal the maximum decrease in intensity was 50%. Because of the high decomposition factor, the second set of data was not highly reliable but we felt was of sufficient accuracy to allow a trial model to be found. All intensities were corrected for background, decomposition, and Lorentz-polarization effects. The absorption coefficient $\mu/\rho = 9.0$ cm^2/g) was low enough to consider absorption corrections unnecessary. Weights were assigned using the method described by Hoard and Jacobson.^{3}

Structure Determination

All atoms are located in general 4-fold positions. The manganese atom was readily located on a three-dimensional Patterson map. The remaining atoms were located with successive electron-density maps.

Refinement was carried out using a modified version of OR FLS.^{4} With all atoms isotropic a reliability index of R = 0.201 was obtained. At this point it was discovered, as had been suspected earlier, that the data collected from the crystal with decomposition of up to 50% were very unreliable. However, since the structure of this molecule appeared to be almost identical to that found in the tetragonal form, it was felt that it was not worthwhile to attempt to retake the second set of data on another crystal. When these data were removed and with anisotropic

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(1) R. J. Angelici and D. L. Denton, *Inorg. Chim. Acta, 2*, 3 (1968).

(2) D. M. Chipman and R. A. Jacobson, *Inorg Chim. Acta, 1*, 393 (1967).

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

(4) W. R. Busing, K. O. Martin, and H. A. Levy, « OR FLS, A FORTRAN CRYSTALLOGRAPHIC LEAST-SQUARES PROGRAM, » ORNL-TM-305 (1962).

Table I. Observed and Calculated Structure Factors (Columns are h, k, F_o and F_c)

h	k	F_o	F_c
L 0			
0	2	1006	979
0	4	307	-301
0	6	621	-628
0	8	193	-168
1	1	556	525
1	2	1297	-1334
1	3	393	-340
1	5	249	235
1	6	67	31
1	8	498	494
2	0	1007	-1050
2	1	367	-341
2	2	480	-417
2	3	458	-411
2	4	78	-80
2	5	208	213
2	8	137	-131
3	1	571	-587
3	2	450	420
3	3	231	-201
3	4	342	355
3	5	218	225
3	6	95	90
3	7	9	-88
3	8	84	-91
4	0	363	-345
4	1	331	336
4	2	274	-251
4	3	916	946
4	4	239	-247
4	5	199	235
4	6	71	-63
4	7	110	-140
4	8	130	138
5	1	551	537
5	2	142	-135
5	4	398	-379
5	5	655	-671
5	7	58	-83
6	0	459	477
6	1	79	-29
6	2	160	151
6	3	621	-626
6	5	117	-84
6	6	216	-136
6	7	402	399
6	8	128	127
7	1	179	-183
7	2	371	-377
7	3	80	-33
7	4	363	-371
7	5	359	358
7	6	200	210
7	7	231	184
8	0	215	-188
8	2	42	-40
8	3	53	74
8	4	248	206
8	5	94	70
8	6	286	307
8	7	180	-134
9	1	114	144
9	2	220	218
9	4	182	194
9	5	138	-124
9	7	164	-150
10	0	80	50
10	4	163	-171
10	5	77	-20
10	6	223	-233
10	7	84	61
11	1	20	56
11	2	135	-111
11	4	112	-95
11	5	76	-123
L 1			
0	1	45	-127
0	2	1028	-911
0	3	184	192
0	4	289	-306
0	5	666	662
0	6	521	537
0	7	309	304
0	8	623	615
1	0	1121	-1131
1	1	75	64
1	2	333	-290
1	3	160	115
1	4	260	251
1	5	167	-138
1	6	355	383
1	7	48	77
2	1	494	-536
2	2	329	349
2	3	415	-398
2	4	682	-651
2	5	406	405
2	6	204	-223
2	7	62	94
2	8	435	-444
3	0	1861	1740
3	1	255	249
3	2	247	-217
3	3	319	329
3	4	380	-391
3	6	393	-383
3	7	110	-117
3	8	171	-175
4	1	565	570
4	2	740	-705
4	3	392	-384
4	4	58	-29
4	5	339	-331
4	6	33	77
4	7	221	-203
4	8	354	329
5	0	48	53
5	1	469	-474
5	2	163	187
5	3	659	-695
5	4	73	97
5	7	310	309
6	1	257	-281
6	2	101	-92
6	3	199	185
6	4	74	6
6	5	472	461
6	6	151	192
6	8	128	138
7	0	301	-297
7	1	204	227
7	2	102	-104
7	3	505	506
7	4	151	154
7	5	139	141
7	6	145	143
7	7	174	-166
8	1	250	271
8	2	130	93
8	3	79	35
8	4	71	-37
8	5	266	-266
8	6	67	-53
8	7	141	-134
9	0	50	85
9	3	141	-171
9	4	102	-125
9	6	89	-140
9	7	109	125
10	1	102	-97
10	2	178	-183
10	3	53	-99
10	4	149	-180
10	6	151	122
10	7	68	-21
11	0	189	-171
11	1	66	-56
11	2	87	-64
11	3	83	-96
L 2			
0	0	529	494
0	1	694	-600
0	2	96	152
0	3	355	348
0	4	424	453
0	6	225	229
0	7	106	-152
0	8	42	-93
1	1	291	256
1	2	351	332
1	3	271	269
1	4	635	657
1	5	267	-276
1	6	323	-314
1	7	116	152
1	8	393	-386
2	0	1058	1018
2	1	69	60
2	2	641	618
2	3	193	-210
2	4	284	-286
2	5	160	165
2	6	425	-435
3	1	301	293
3	2	659	-662
3	4	193	-214
3	5	58	-60
3	6	399	418
3	7	160	-150
3	8	464	463
4	0	671	-833
4	1	234	-218
4	2	286	-285
4	3	261	-262
4	4	162	183
4	6	181	200
4	7	324	311
4	8	101	-84
5	1	708	-723
5	2	217	213
5	3	52	-74
5	4	128	-143
5	5	472	506
5	6	49	27
5	7	75	116
5	8	128	-139
6	0	300	306
6	1	309	333
6	2	216	-219
6	3	487	503
6	4	93	-95
6	5	100	155
6	6	75	-107
6	7	163	-129
6	8	149	-166
7	1	306	325
7	2	178	-183
7	3	74	-116
7	4	24	-38
7	5	148	-151
7	6	46	-42
7	7	62	-92
8	0	180	169
8	1	209	-191
8	2	185	163
8	3	307	-301
8	4	94	88
8	6	41	65
8	7	106	106
9	1	79	-72
9	2	176	-196
9	3	21	80
9	4	123	-157
9	5	148	144
9	6	62	66
9	7	84	-12
10	0	352	-346
10	1	89	41
10	2	192	-167
10	3	88	69
10	4	155	141
10	5	80	-6
L 3			
0	1	135	155
0	2	310	288
0	3	96	-30
0	4	479	494
0	5	198	-206
0	6	59	24
0	7	166	-195
0	8	59	-54
1	0	215	216
1	1	161	-200
1	3	253	-246
1	4	470	-474
1	5	72	-65
1	6	355	-339
1	7	283	307
1	8	74	-59
2	1	178	-216
2	2	605	-614
2	3	64	-89
2	4	326	-325
2	5	460	468
2	6	176	177
2	7	52	129
2	8	453	439
3	0	383	-346
3	1	419	-433
3	2	188	-209
3	3	114	-106
3	4	453	455
3	5	94	-42
3	6	423	421
3	7	50	52
4	1	354	-374
4	2	210	232
4	3	107	103
4	4	247	265
4	5	158	170
4	6	348	-338
4	7	168	164
4	8	409	-405
5	0	350	356
5	1	148	170
5	2	169	161
5	3	105	145
5	4	242	-233
5	5	20	38
5	6	329	-338
5	7	259	-238
5	8	103	-122
6	1	192	157
6	2	250	-262
6	3	123	-103
6	4	88	-96
6	5	209	-192
6	6	171	152
6	7	173	-166
6	8	253	263
7	0	140	-78
7	1	95	-109
7	2	86	55
7	3	111	-103
7	4	127	137
7	5	79	58
7	6	68	66
7	7	208	196
8	1	126	-121
8	3	159	171
8	4	156	-147
8	5	318	325
8	6	24	29
8	7	90	77
9	0	134	-142
9	1	196	167
9	2	169	-149
9	3	269	223
9	4	124	107
9	5	60	2
9	6	122	136
L 4			
0	0	149	-156
0	1	400	-416
0	3	512	-535
0	4	131	-207
0	5	185	-163
0	7	380	386
0	8	67	-47
1	1	398	-384
1	2	306	-322
1	3	63	20
1	4	129	-236
1	5	140	169
1	6	155	161
1	8	163	183
2	0	191	-203
2	1	102	99
2	2	25	-29
2	3	152	171
2	4	510	500
2	5	185	168
2	6	350	336
2	7	134	-148
2	8	90	-81
3	1	194	177
3	2	415	411
3	3	227	230
3	4	438	437
3	5	148	125
3	6	129	-136
3	7	80	-38
3	8	267	-260
4	0	417	447
4	1	67	16
4	2	276	269
4	3	77	13
4	4	224	-205
4	5	134	-126
4	6	300	-294
4	7	67	-93
4	8	50	-37
5	1	134	-115
5	2	251	-249
5	3	145	-143
5	4	198	-179
5	5	67	47
5	6	54	53
5	8	207	200
6	0	260	-274
6	1	156	-148
6	2	225	-224
6	5	72	59
6	6	50	67
6	7	136	135
6	8	154	-105
7	1	272	-271
7	2	92	46
7	4	76	71
7	5	221	216
7	6	118	-68
7	7	157	109
8	0	123	54
8	1	195	172
8	2	133	53
8	3	248	253
8	4	115	61
8	5	47	47
L 5			
0	1	409	-431
0	2	29	14
0	3	159	142
0	4	86	39
0	5	331	315
0	6	52	-39
0	7	56	120
0	8	26	46
1	0	375	-398
1	1	230	210
1	2	151	-121
1	3	365	357
1	4	107	44
1	5	40	71
1	6	126	130
1	7	270	-244
2	1	197	159
2	2	335	331
2	3	96	10
2	4	303	315
2	5	214	-199
2	8	117	-145
3	0	208	195
3	1	161	-148
3	2	156	153
3	3	176	-191
3	4	62	-116
3	5	81	-88
3	6	138	-148
3	7	171	161
3	8	71	64
4	1	128	-103
4	2	207	-226
4	4	221	-214
4	5	137	116
4	6	36	16
4	7	84	102
4	8	98	79
5	0	198	-207
5	2	108	-111
5	3	40	-49
5	4	161	153
5	5	97	-13
5	6	168	119
5	7	88	-68
6	1	202	-209
6	2	151	156
6	3	76	9
6	4	151	154
6	5	123	105
L 6			
0	1	160	164
0	2	102	-91
0	3	223	236
0	4	47	-82
0	5	81	-37
0	6	81	8
0	7	242	-236
0	8	78	-34
1	1	160	149
1	2	77	-17
1	3	158	-140
1	4	79	9
1	5	331	-326
1	6	95	-43
1	7	223	-190
1	8	84	-62
2	0	70	35
2	1	153	-149
2	2	66	29
2	3	179	-188
2	4	50	-29
2	5	63	-6
2	6	143	-126
2	7	154	158
3	1	142	-114
3	2	84	-52
3	3	137	133
3	4	66	-20
3	5	186	166
4	0	97	-93
4	1	93	63
4	2	98	46
4	3	60	81

Table IIa. Final Atomic Parameters (Standard Errors × 10^4 are given in parentheses)

Atom	x	y	z
Mn	0.1982(3)	0.0956(3)	0.2981(5)
O1	0.1161(19)	−0.0674(15)	0.4432(27)
O2	0.4377(14)	0.0807(11)	0.5681(25)
O3	0.3151(21)	0.2273(14)	0.0607(36)
O4	0.1162(22)	0.1983(12)	0.6468(34)
O5	0.1687(15)	0.1949(11)	−0.1151(23)
N1	0.0257(14)	0.1126(12)	0.1038(23)
N2	0.3461(20)	−0.0333(14)	0.0719(37)
C1	0.1374(29)	−0.0003(27)	0.3997(49)
C2	0.3437(19)	0.0837(16)	0.4575(34)
C3	0.2676(26)	0.1730(27)	0.1537(41)
C4	0.1479(31)	0.1619(22)	0.5091(46)
C5	−0.0328(22)	0.1974(19)	0.0915(41)
C6	0.2390(21)	0.0215(16)	0.0546(35)
C7	0.3637(28)	−0.0895(22)	−0.0852(45)

temperature factors for Mn, N, and O, a final $R = 0.098(\Sigma||F_o|-|F_c||/\Sigma|F_o|)$ and weighted $R\omega = 0.077[(\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2)^{1/2}]$ were obtained. With only 467 reflections left for refinement it seemed unrealistic to refine with anisotropic temperature factors for carbon. A final difference Fourier was calculated and no peaks greater than 0.3 electrons/Å^3 were found. The observed and calculated structure factors are given in Table I.[5] The final positional parameters, temperature factors, and standard errors are given in Tables IIa and IIb.

Molecular Structure

As in the tetragonal form each manganese atom is surrounded by four carbonyl groups, one methyl amine, and one N-methyl carboxamido group in an essentially octahedral configuration (see Figure 1). Bond lengths and angles were calculated with OR FFE[6] and are compared with those in the tetragonal form in Table III and IV. All bonds except C6–N2 and N2–C7 and all angles except C1–Mn–C2 of the monoclinic form are within three standard deviations of the corresponding parameters in the tetragonal form. Even these differences may not be real as the standard deviations represent a lower limit to the actual error. Therefore it is concluded that the two molecules are essentially identical. This can better be appreciated by comparing the drawings of the two molecules in Figure 1. (All drawings except

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[5] Observed structure factors from the second crystal are available from the authors.

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

Table IIb.. Final Anisotropic Temperature Coefficients $^a \times 10^5$ (Standard errors $\times 10^5$ in parentheses) and Isotropic Temperature Coefficients (Standard errors $\times 10^2$ in parentheses)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{33}	Atom	B
Mn	674(34)	376(31)	1461(9)	−70(33)	−11(63)	27(57)	C1	4.06(60)
O1	1621(252)	496(178)	2142(561)	−58(194)	536(448)	−49(263)	C2	3.28(42)
O2	1258(184)	663(128)	4027(602)	14(143)	−1480(362)	−50(237)	C3	3.95(58)
O3	1852(290)	419(181)	4593(827)	−360(186)	−189(543)	268(302)	C4	4.48(60)
O4	2256(374)	425(166)	4641(877)	75(206)	−301(652)	139(291)	C5	4.63(49)
O5	1130(211)	645(120)	2092(498)	180(139)	−377(375)	114(200)	C6	2.72(41)
N1	721(184)	331(139)	1422(485)	216(136)	103(356)	−330(217)	C7	5.91(57)
N2	1080(268)	435(199)	4278(985)	−14(186)	−204(592)	124(337)		

^{a} Anisotropic temperature expression form 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. Bond Lengths in Monoclinic and Tetragonal Forms of $Mn(CO)_4(NH_2CH_3)(CONHCH_3)$(Standard deviations $\times 10^3$ in parentheses)

Atoms	Monoclinic	Tetragonal
Mn-C1	1.815(36)Å	1.856(12)Å
Mn-C2	1.762(13)	1.775(13)
Mn-C3	1.756(36)	1.839(13)
Mn-C4	1.832(34)	1.845(12)
Mn-N1	2.110(11)	2.111(8)
C1-O1	1.138(30)	1.124(11)
C2-O2	1.156(13)	1.148(11)
C3-O3	1.196(31)	1.146(11)
C4-O4	1.131(36)	1.135(11)
N1-C5	1.492(26)	1.148(12)
C6-O5	1.228(15)	1.251(10)
C6-N2	1.443(27)	1.345(12)
N2-C7	1.366(34)	1.470(12)

Table IV. Bond Angles in Monoclinic and Tetragonal Forms of $Mn(CO)_4(NH_2CH_3)(CONHCH_3)$(Standard deviations $\times 10^1$ in parentheses)

Atoms	Monoclinic	Tetragonal
Mn-C1-O1	166.9(37)°	174.9(10)°
Mn-C2-O2	175.6(19)	176.5(10)
Mn-C3-O3	178.0(27)	174.4(11)
Mn-C4-O4	175.6(29)	175.2(9)
Mn-N1-C5	118.9(10)	121.1(7)
Mn-C6-O5	120.1(15)	121.2(7)
Mn-C6-N2	123.1(12)	121.4(7)
O5-C6-N2	116.7(20)	117.4(8)
C6-N2-C7	121.9(16)	122.4(8)
C1-Mn-C3	116.7(15)	167.8(4)
C2-Mn-N1	178.6(10)	178.3(4)
C4-Mn-C6	175.3(9)	175.7(4)
C1-Mn-C2	92.5(10)	87.2(5)
C1-Mn-C4	94.6(16)	96.2(5)
C1-Mn-N1	88.9(8)	91.1(4)
C1-Mn-C6	84.0(13)	84.7(4)
C3-Mn-C4	98.7(14)	95.2(5)
C3-Mn-N1	90.8(7)	92.8(4)
C3-Mn-C6	82.8(13)	84.2(4)
C4-Mn-N1	91.3(8)	91.6(14)
N1-Mn-C6	84.2(6)	84.1(4)

Figure 3 were made by OR TEP.)[7] Due to the greater accuracy in the structure determination of the tetragonal form, the molecular parameters listed for it should probably be considered more reliable and used in future comparisons with similar molecules.

As in the tetragonal form the manganese to carbonyl bond distances are reasonable. The carbonyl opposite the NH_2CH_3 group has a shortened bond due to the *trans* effect of the NH_2CH_3 group. The carbonyl carbon-oxygen distances are all normal to within three standard deviations. There are no intra-molecular hydrogen bonds. The Mn, C6, O5, N2 and C7 atoms all lie within 0.05 Å of their least-squares plane. The planarity of this group and the fact that all bond angles are approximately 120° indicate that C6 and N7 are essentially sp^2 hybridized. The plane containing the N-methylcarboxamido group is tilted about 12° from the plane containing C2, C4, and N1 as compared to 9° in the tetragonal form.

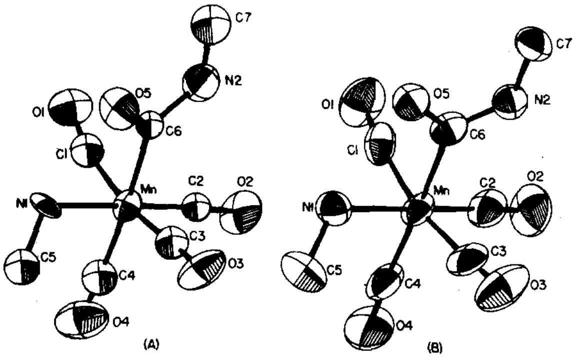

Figure 1. $Mn(CO)_4(NH_2CH_3)(CONHCH_3)$ molecule in (a) monoclinic and (b) tetragonal crystals.

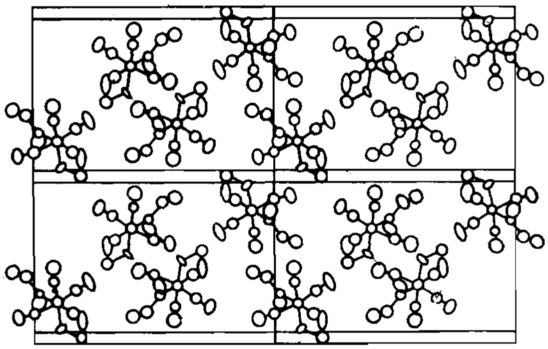

Figure 2. Packing of monoclinic $Mn(CO)_4(NH_2CH_3)(CONHCH_3)$ viewed along c axis.

Thus the molecule in the monoclinic form is also six-coordinated and essentially identical to the molecule in the tetragonal form. This does not rule out the possibility of a seven-coordinated species in solu-

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(7) C. K. Johnson, « OR TEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations », ORNL-3794, Revised (1965).

tion but apparently such a species does not exist in the solid state.

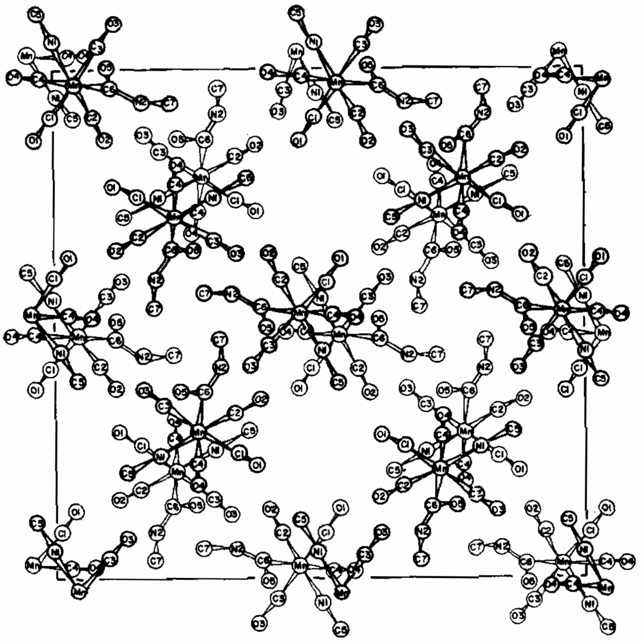

Figure 3. Packing of tetragonal $Mn(CO)_4(NH_2CH_3)(CONHCH_3)$ viewed along c axis.

Crystal Structure

Of considerable interest is the fact that $Mn(CO)_4(NH_2CH_3)(CONHCH_3)$ crystallizes in two different forms. The space group for the tetragonal form is $I4_1/a$ with 16 molecules per unit cell compared to the monoclinic form with space group $P2_1/n$ and 4 molecules per unit cell. The tetragonal crystals have much higher symmetry and since the molecule itself has C_1 symmetry, it would be expected that the packing would be less efficient than in the lower symmetry space group. This is readily observed when one compares densities and volumes. The calculated density (1.45 g/cm^3) of the tetragonal form is less than the calculated density (1.59 g/cm^3) of the monoclinic form. Also the volume for 16 molecules in the tetragonal form is 4714 $Å^3$ compared to a volume for 16 molecules in the monoclinic form of 4296 Å.[3] The packing diagrams in Figures 2 and 3 show relatively large holes in the tetragonal structure while the monoclinic structure is more closely packed.

In considering the possible forces which might be responsible for the packing arrangement found in this study, it was noticed that the N1–O5′ distance (05′ being related to 05 by a center of symmetry) of 2.98 Å is short enough to be typical of a weak hydrogen bond. A normal linear N–O hydrogen bond distance is approximately 2.8 Å. Also the C5–N1–O5′ and Mn–N1–05′ angles are 110° and 118°, respectively, indicating an approximate tetrahedral configuration of the nitrogen atom in the NH_2CH_3 group. Thus as can be seen in Figure 4, pairs of molecules related by a center of symmetry are held together by two of these hydrogen bonds. This same configuration is also present in the tetragonal form although it was previously overlooked. In the tetragonal form the C5–N1–O5′ angles are both 110°. The Mn atoms approach each other most closely through this center of symmetry with the Mn–Mn distance 6.05 Å in the tetragonal case and 6.13 Å in the monoclinic case.

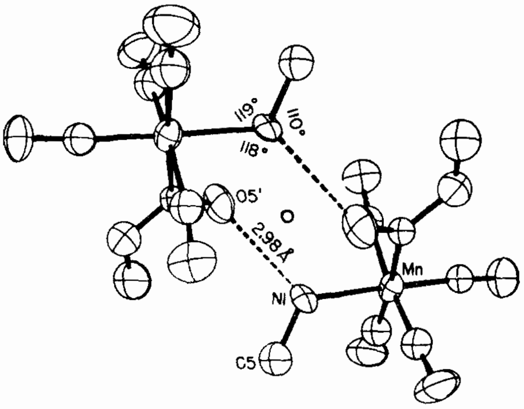

Figure 4. Hydrogen bonding in monoclinic $Mn(CO)_4(NH_2CH_3)(CONHCH_3)$.

There appear to be no other similarities between the two structures and the packing of these pairs of molecules must thus be determined only by van der Waals forces. This is consistent with the fact that both forms of crystals were grown simultaneously by sublimation at a temperature slightly above room temperature[8] indicating that the crystal packing forces are weak and that the two forms must have about the same lattice energy.

(8) R. J. Angelici, private communication.