ACTA CHEMICA SCANDINAVICA 27 (1973) 3513–3522

The Crystal and Molecular Structure of *cis*-Dichloro-bis(1,2-ethanediol)manganese(II) $[MnCl_2(C_2H_6O_2)_2]$

BRITT-MARIE ANTTI

Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

The crystal structure of $[MnCl_2(C_2H_6O_2)_2]$ has been determined and refined from three-dimensional X-ray diffraction data. The crystals are monoclinic, space group $P2_1/c$, with the following cell dimensions and their estimated standard deviations; $a = 9.491 \pm 0.001$ Å, $b = 7.223 \pm 0.001$ Å, $c = 14.213 \pm 0.001$ Å and $\beta = 92.229 \pm 0.007°$. There are four formula units per unit cell and each atom occupies a general fourfold position. The intensity material was collected with the Weissenberg equi-inclination technique from the *b*-axis using a linear diffractometer and Mo$K\alpha$-radiation. With anisotropic temperature factors for all the non-hydrogen atoms the refinement terminated at a final conventional *R*-value of 0.053. The Mn^{2+} ion is octahedrally surrounded by the four glycol * oxygens and the two chlorine atoms. In this way neutral molecules $[MnCl_2(C_2H_6O_2)_2]$ are formed and these are held together through hydrogen bonds of the type O–H···Cl. A tentative proposal for the positions of the hydrogen atoms is given.

An investigation of complexes between polyols and divalent transition metal ions is currently in progress in this department. The first work in this series, a crystal structure determination of $[Cu(C_2H_6O_2)_3]SO_4$, was recently published by the author.[1] The crystal structure determination $[MnCl_2(C_2H_6O_2)_2]$ which is presented below forms the second paper in the series.

EXPERIMENTAL

Crystal preparation and analyses. The crystals were prepared by dissolving 7.5 g $MnCl_2.4H_2O$ in 7 g glycol by heating on a water bath. The solution obtained was placed over sulphuric acid *in vacuo*. Pink crystals, in the form of somewhat irregular hexagonal plates, separated after a short time. The chlorine content of the crystals was determined gravimetrically to be 27.14 %. (Calculated for $[MnCl_2(C_2H_6O_2)_2]$, 28.36 %.) No other analyses were made.

Crystal data and space group. From rotation photographs around the *a*- and *b*-axes and the corresponding Weissenberg photographs (zero- and first layers) it was concluded

* Throughout this paper 1,2-ethanediol will be referred to as glycol.

that the crystals are monoclinic. The cell dimensions were refined from a powder photograph taken in a camera of Guinier-Hägg type and with Si as internal standard. (To avoid fluorescence the Cu$K\alpha$-radiation was filtered through copper foil before being diffracted in the crystal powder.) The following parameters and their corresponding standard deviations were obtained $a = 9.491 \pm 0.001$ Å, $b = 7.223 \pm 0.001$ Å, $c = 14.213 \pm 0.001$ Å and $\beta = 92.229 \pm 0.007°$. The density of the crystals was determined by the flotation method using bromoform and xylene. The experimental value was 1.68 g/cm³ and the value calculated for four formula units in the unit cell was 1.70 g/cm³. Systematic extinctions were found for $h0l$ when l is odd and for $0k0$ when k is odd. This is characteristic for the space group $P2_1/c$ (No. 14).[2]

Intensity data. The intensities from the crystal $[MnCl_2(C_2H_6O_2)_2]$ were collected and measured with an automatic linear diffractometer, PAILRED, and Mo$K\alpha$-radiation. The crystal used was hygroscopic and therefore it was enclosed in a capillary of Lindeman glass during the measurements. It was rotated around the b-axis and intensities for $h0l - h8l$ were measured. Reflexions with a total number of counts less than 4000 during one scan interval were measured twice. The half-scan interval for reflexions with $\theta \geq 22°$ (Ω_1) varied between $0.9° - 1.2°$ and for those with $\theta \leq 22°$ (Ω_2) between 1.8° and 2.1° for $h0l - h3l$. From $h3l$ to $h8l$, Ω_1 was 1.2° and Ω_2 was 2.1°. The scan speed used was 1°/min. Background intensities, B_1 and B_2, were measured during 40 sec (t_B) before and after each scan. The intensity for a reflexion, TI, was calculated from the measured total intensity, T, (peak + background) by subtracting the background counts B_1 and B_2 according to the relation

$$TI = T/TN - [t_T/(t_B/60)](B_1 + B_2)$$

where t_T stands for the total scanning time $[\Omega_{1 \text{ or } 2}/(\text{scan speed/min})]$ and TN is the number of times the reflexion is measured. The relative counting statististical error of each reflexion $\Delta T/TI$, was calculated using the formula

$$\frac{\Delta T}{TI} = \frac{[T/TN^2 + t^2(B_1 + B_2) + T^2/TN^2 \times 0.0001]^{1/2}}{T/TN - t(B_1 + B_2)}$$

where $t = t_T/(t_B/60)$ and $T^2/TN^2 \times 0.0001$ is a term that corrects for the linear error in the diffractometer. Out of a total of 3291 measured intensities those with $\Delta T/TI > 0.5$ were omitted leaving 1969 independent reflexions for the refinement.

Besides the normal correction for Lorentz and polarization factors absorption correction was also made. The linear absorption coefficient was 19.1 cm^{-1} and the greatest difference in transmission was 18 %. When the refinement was terminated, structure factors for all the omitted reflexions within the copper sphere were calculated. These were all weak reflexions, weaker or equal to the threshold value of the intensity material.

The diffractometer data correction program used was the modified version of a program originally written by Ivarsson and Lundberg.[3] The computer programs used were the same as described by Antti and Lundberg.[4]

STRUCTURE DETERMINATION AND REFINEMENT

The manganese and chlorine atoms were located from a three-dimensional Patterson synthesis, and all the other atoms were found by standard Fourier methods.

The atomic parameters and the atomic temperature factors were refined by full matrix least-squares techniques. The reflexion material was weighted according to the method proposed by Cruickshank,[5] with $a = 50$, $c = -0.015$ and $d = 0.0001$. The atomic scattering factors for Mn^{2+}, Cl^-, O, and C were used and taken from the International Tables [6] and account was taken of the real parts of the dispersion corrections for the manganese and the chlorine atoms. With isotropic temperature factors for all atoms the refinement converged to a conventional R-value of 0.083. A final refinement including

anisotropic temperature factors for all atoms resulted in a final R-value of 0.053. All parameter shifts in the last refinement were less than 10 % of the estimated standard deviations.

Finally a difference Fourier synthesis was calculated. From the twenty highest peaks which appeared in this map twelve corresponded to reasonable positions for the twelve independent hydrogen atoms in general positions. Four of the hydrogen atoms, those bound to oxygen atoms, were suitably located for hydrogen bonding to chlorine atoms.

After two cycles of least-squares refinement of the positional parameters for all the hydrogen atoms the R-value decreased to 0.046. During this refinement the isotropic thermal parameters of the hydrogen atoms and the positional and anisotropic thermal parameters of all the other atoms were kept constant. The scattering factors for the hydrogen atoms used were those proposed by Stewart, Davidson and Simpson.[7] When the non-hydrogen atoms were refined in two further cycles, while the hydrogen atom positions were kept constant, there was a further decrease in the R-value to 0.044.

The significance of this decrease in R-value from 0.053 to 0.044 was tested by a method proposed by Hamilton (1965)[8] and somewhat simplyfied by Pawley (1970).[9] The decrease proved to be significant with more than 99 % certainty. The present material gave an R-ratio of 1.205 which should be compared with the calculated ratio $\mathcal{R}_{48,1821,0.01} = 1.017$. The indices 48, 1821, and 0.01 refer to the dimension of the hypothesis, the degrees of freedom, and the significance level, respectively. Although the determination of the hydrogen atom positions cannot be considered especially accurate, the introduction of them made the values of the estimated standard deviations for all the non-hydrogen atoms 16 to 23 % lower.

Under these circumstances it seems to be justified to include the hydrogen atom positions. A last difference Fourier map was then calculated in which no abnormalities could be detected. A list of the final positional parameters and the thermal parameters is given in Tables 1 *a* and 1 *b*. The observed and calculated structure factors are listed in Table 2.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure is built up from discrete molecules $[MnCl_2(C_2H_6O_2)_2]$, which are held together through weak hydrogen bonds and van der Waals contacts. The hydrogen bonds are of the type Cl···O – H. A drawing illustrating the packing and the hydrogen bond contacts is shown in Fig. 1.

In the molecule $[MnCl_2(C_2H_6O_2)_2]$ manganese(II) coordinates to four oxygen atoms and two chlorine atoms in a somewhat distorted octahedral arrangement as can be seen in Fig. 2. The chlorine atoms, which are in *cis*-positions, are at nearly equal distances, 2.463 Å and 2.464 Å, respectively, from the manganese atom. The distances between the oxygen and manganese atoms are very similar and lie between 2.184 Å and 2.247 Å. The angles within the octahedron show a rather wide variation around the ideal value. For example, the angles that should be 90° in a regular octahedron, *i.e.* the angles $L-M-L$ where the L:s stand for ligands in adjacent corners and M is the

Table 1a. The atomic positional fractional coordinates and the anisotropic thermal parameters. All values have been multiplied by 10^4. (Standard deviations for the last significant figure are given in parentheses). Anisotropic temperature factors have been calculated according to the formula exp $[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	2510(1)	1621(1)	4293(0.4)	62(1)	108(1)	30(0.3)	−10(1)	− 4(1)	3(1)
Cl(1)	2062(1)	1399(2)	5984(1)	101(1)	197(2)	29(0.4)	−44(3)	5(1)	1(2)
Cl(2)	2981(1)	6680(1)	9004(1)	100(1)	107(2)	50(1)	−7(2)	−6(1)	1(2)
O(11)	4586(3)	2841(5)	4587(2)	74(3)	210(8)	38(2)	−44(8)	−13(3)	14(5)
O(12)	3430(3)	2324(5)	2904(2)	104(4)	188(7)	29(1)	−44(8)	−4(3)	34(5)
O(21)	1583(3)	4463(4)	4231(2)	87(3)	126(6)	57(2)	8(7)	−7(4)	10(5)
O(22)	371(3)	1362(5)	3657(2)	70(3)	164(7)	54(2)	−29(7)	−21(4)	4(5)
C(11)	4536(5)	8155(8)	1203(4)	72(5)	229(12)	57(3)	42(12)	24(5)	−12(9)
C(12)	4513(5)	3715(7)	2987(3)	103(5)	165(10)	48(2)	−15(11)	42(6)	35(7)
C(21)	448(6)	4623(8)	3550(4)	119(7)	182(12)	63(3)	97(14)	−23(7)	16(9)
C(22)	494(5)	8005(8)	1326(4)	74(5)	234(14)	78(4)	−61(12)	−19(7)	23(10)

Table 1 b. Atomic positional fractional coordinates for the hydrogen atoms. All values have been multiplied by 10^3. (Standard deviations for the last significant figure are given in parentheses). The thermal parameters have not been refined.

	x	y	z	B
H(O11)	506(5)	258(8)	12(4)	4.0
H(O12)	298(5)	238(8)	236(3)	4.0
H(O21)	207(5)	574(8)	423(3)	4.0
H(O22)	12(5)	537(8)	110(3)	4.0
H(C11)1	409(6)	683(9)	138(4)	5.0
H(C11)2	381(6)	914(9)	108(4)	5.0
H(C12)1	406(6)	497(9)	310(4)	5.0
H(C12)2	501(6)	381(8)	243(4)	5.0
H(C21)1	89(6)	467(9)	281(4)	5.0
H(C21)2	−11(6)	589(9)	363(4)	5.0
H(C22)1	94(6)	807(9)	70(4)	5.0
H(C22)2	126(6)	806(9)	180(4)	5.0

central atom, vary between 72.4° and 104.7°. For a complete list of distances and angles within the octahedron, see Table 3.

A comparison can be made between $[MnCl_2(C_2H_6O_2)_2]$, the subject of this report, and the structure of $MnCl_2.4H_2O$.[10] It is interesting to observe that the manganese atom has retained its configuration although water has been substituted by glycol. In $MnCl_2.4H_2O$ there are also discrete molecules or octahedra where the manganese atom coordinates two chlorine atoms at an average distance of 2.488 Å and four oxygen atoms at an average distance of 2.206 Å. These distances should be compared with those obtained from the structure $[MnCl_2(C_2H_6O_2)_2]$, which are 2.464 Å and 2.215 Å respectively. The average Mn−Cl distance of 2.464 Å in the glycol compound is significantly shorter

Table 2. Observed and calculated structure factors (× 10). Values marked with an asterisk were not included in the refinements.

H	L		
K=	0		
13	2	157	155
13	-2	105	89
12	-8	190	178
12	-6	105	90
12	-4	131	144
11	6	131	134
11	4	92	94
11	2	121	122
11	-2	172	167
11	-4	234	235
11	-6	103	97
11	-8	154	155
11	-10	136	126
10	-10	133	121
10	-8	157	146
10	-4	70	49
10	0	245	251
10	2	123	115
10	4	125	126
10	8	214	222
10	10	218	218
9	12	185	185
9	10	68	91
9	8	89	87
9	6	146	150
9	4	343	343
9	2	238	251
9	-2	312	311
9	-4	191	187
9	-6	173	167
9	-8	58	54
9	-10	248	240
9	-12	77	64
8	-16	160	148
8	-14	120	105
8	-12	66	25*
8	-10	143	134
8	-8	117	116
8	-6	164	162
8	-4	70	49
8	-2	172	166
8	0	56	55
8	2	451	459
8	4	350	370
8	6	384	394
8	8	456	464
8	10	210	214
8	12	175	178
8	14	263	270
7	14	64	11*
7	12	149	153
7	10	227	227
7	8	84	86
7	6	112	109
7	4	352	348
7	-2	210	210
7	-4	337	339
7	-8	168	171
7	-10	289	280
7	-12	143	136
7	-16	131	108
6	-16	199	189
6	-12	135	118
6	-10	78	76
6	-8	79	58
6	-6	224	222
6	-4	483	476
6	-2	136	121
6	0	233	251
6	2	690	694
6	4	363	358
6	6	242	236
6	8	577	582
6	10	218	224
6	12	351	357
6	14	268	268
5	16	77	68
5	12	211	201
5	10	251	248
5	8	140	132
5	6	252	257
5	4	334	332
5	2	411	405
5	-2	372	371
5	-4	622	614
5	-6	285	288
5	-8	55	39
5	-10	308	304
5	-12	272	265
5	-16	134	139
5	-18	97	107
4	-18	87	86
4	-16	144	124
4	-12	55	59
4	-10	112	112
4	-8	239	217
4	-6	46	2*
4	-4	604	594
4	-2	124	112
4	0	1170	1159
4	2	1312	1317
4	4	403	394
4	6	1050	1062
4	8	631	629
4	12	367	364
4	14	247	237
4	16	59	22*
4	18	131	120
3	18	204	191
3	16	105	101
3	14	119	123
3	12	156	158
3	10	378	391
3	8	421	417
3	6	142	138
3	4	923	933
3	2	864	855
3	-4	541	545
3	-6	232	239
3	-10	399	402
3	-12	343	343
3	-16	124	137
3	-18	200	198
2	-18	138	146
2	-12	238	229
2	-10	336	323
2	-8	217	226
2	-6	1496	1493
2	-4	384	393
2	-2	385	368
2	0	831	848
2	2	1200	1219
2	4	377	368
2	6	1121	1127
2	8	885	889
2	10	459	457
2	12	662	658
2	14	142	144
2	16	106	90
2	18	87	101
1	18	130	133
1	16	220	217
1	12	224	217
1	10	525	529
1	8	100	100
1	6	677	648
1	4	82	71
1	2	1099	1069
1	-4	1406	1436
1	-6	581	571
1	-8	511	517
1	-10	301	290
1	-12	474	481
1	-14	153	142
1	-16	186	193
1	-18	183	178
0	4	1491	1522
0	6	1337	1333
0	8	340	335
0	10	345	329
0	12	139	116
0	14	147	138
0	16	62	59
K=	1		
12	4	181	186
12	2	112	124
12	0	60	65
12	-2	99	119
12	-4	123	130
12	-8	93	129
11	-8	97	104
11	-6	164	168
11	-5	64	70
11	-3	79	87
11	-2	71	50
11	0	159	164
11	2	83	98
11	3	59	58
11	5	57	57
11	6	90	83
11	8	159	151
10	11	66	33*
10	9	110	122
10	8	114	124
10	7	69	69
10	4	203	204
10	3	78	86
10	2	389	398
10	-1	53	39
10	-2	453	451
10	-4	308	309
10	-8	193	216
10	-9	75	89
10	-10	97	107
9	-14	62	71
9	-11	87	92
9	-9	52	64
9	-8	169	184
9	-6	95	85
9	-5	122	127
9	-4	79	80
9	-3	140	139
9	-2	145	148
9	0	338	347
9	1	112	108
9	2	172	176
9	3	123	130
9	6	270	275
9	8	159	165
9	9	62	53
9	10	89	79
8	15	87	92
8	13	124	126
8	12	62	47
8	10	95	87
8	9	157	161
8	8	253	252
8	7	197	195
8	6	70	73
8	5	50	7*
8	4	329	335
8	3	147	141
8	2	329	317
8	1	177	183
8	0	234	227
8	-2	261	254
8	-3	72	52
8	-4	401	385
8	-6	132	148
8	-8	176	191
8	-9	84	91
8	-10	359	353
8	-11	91	106
8	-14	102	124
8	-15	74	106
8	-16	60	109*
7	-16	75	108
7	-14	60	92
7	-12	91	107
7	-11	154	170
7	-9	178	192
7	-8	134	137
7	-7	118	126
7	-6	264	273
7	-5	257	257
7	-4	243	245
7	-3	208	209
7	-2	210	212
7	0	203	208
7	1	169	168
7	2	214	217
7	3	193	196
7	4	78	69
7	5	180	181
7	6	281	280
7	8	133	136
7	9	129	125
7	10	55	54
7	11	102	100
7	12	165	161
7	14	124	135
7	16	86	74
6	15	77	102
6	14	77	62
6	13	246	244
6	12	59	41
6	11	77	82
6	9	253	255
6	8	69	64
6	7	422	431
6	6	192	190
6	5	177	178
6	3	344	346
6	2	348	360
6	1	357	352
6	0	370	355
6	-1	154	159
6	-2	308	320
6	-3	131	128
6	-4	875	858
6	-5	153	162
6	-6	305	287
6	-8	257	278
6	-10	419	481
6	-12	155	189
6	-14	54	95*
6	-16	115	135
6	-17	80	87
5	-17	93	106
5	-16	78	80
5	-15	60	68
5	-14	78	96
5	-13	67	48
5	-12	103	101
5	-11	197	213
5	-10	117	124
5	-9	149	168
5	-8	313	322
5	-7	98	87
5	-6	386	381
5	-5	217	227
5	-4	49	54
5	-3	468	468
5	-2	475	474
5	-1	130	122
5	0	495	499
5	1	137	139
5	2	409	405
5	3	410	408
5	5	177	183
5	6	185	187
5	8	324	330
5	9	92	96
5	10	171	176
5	11	163	167
5	12	132	131
5	13	96	90
5	14	100	119
5	17	72	84
4	18	143	160
4	15	58	69
4	14	249	256
4	13	215	222
4	12	193	192
4	11	201	206
4	9	256	256
4	8	99	107
4	7	562	558
4	6	171	162
4	5	301	306
4	4	176	177
4	3	505	507
4	2	701	684
4	1	944	929
4	0	567	562
4	-1	150	166
4	-2	105	98
4	-3	414	416
4	-4	712	724
4	-5	522	523
4	-6	556	537
4	-7	104	122
4	-8	144	139
4	-9	129	138
4	-10	409	452
4	-12	296	368
4	-14	68	83
4	-16	178	223
4	-18	101	142
3	-17	87	105
3	-15	76	99
3	-14	137	153
3	-13	85	101
3	-12	220	238
3	-11	201	212
3	-10	82	95
3	-9	184	197
3	-8	177	192
3	-6	417	423
3	-5	250	256
3	-4	59	7*
3	-3	199	201
3	-2	338	341
3	-1	443	455
3	0	507	502
3	2	396	395
3	3	230	224
3	4	594	577
3	5	387	388
3	6	526	534
3	7	270	268
3	8	333	341
3	9	165	165
3	11	168	185
3	12	153	168
3	13	89	103
3	14	175	186
3	16	142	150
3	17	83	83
3	19	73	75
2	18	195	216
2	17	64	63
2	16	139	148
2	14	160	175
2	13	151	161
2	12	261	262
2	11	172	167
2	10	287	299
2	9	138	140
2	8	238	231
2	7	621	622
2	6	336	344
2	5	342	337
2	4	469	451
2	3	336	325
2	2	355	365
2	1	1127	1131
2	0	214	223
2	-1	601	582
2	-2	1060	1070
2	-3	674	684
2	-4	758	775
2	-5	552	571
2	-6	886	935
2	-7	116	120
2	-8	152	163
2	-9	184	191
2	-10	517	577
2	-11	146	164
2	-12	485	566
2	-16	187	232
2	-18	141	197
1	-17	96	103
1	-16	52	70
1	-14	244	275
1	-12	60	54
1	-11	152	159
1	-10	76	80
1	-9	121	130
1	-8	471	474
1	-6	964	956
1	-5	75	94
1	-4	68	79
1	-3	224	213
1	2	263	242
1	3	125	126
1	4	137	126
1	5	225	225
1	6	90	112
1	7	85	72
1	8	591	586
1	11	162	173
1	12	165	180
1	13	177	205
1	14	184	202
1	17	91	101
1	18	67	71
1	19	78	86
0	18	177	194
0	16	213	236
0	14	245	261
0	13	91	77
0	12	506	525
0	11	192	202
0	10	127	133
0	9	120	120
0	8	282	272
0	7	292	295
0	6	747	732
0	5	685	688
0	3	86	84
K=	2		
12	5	145	143
12	3	213	212
12	-1	178	168
12	-3	196	195
12	-7	100	78
11	-9	75	61
11	-7	88	94
11	-6	76	55
11	-5	67	69
11	-1	136	123
11	1	99	99
11	3	64	59
11	7	134	141
11	9	109	105
10	11	67	60
10	9	142	136
10	7	113	125
10	5	64	81
10	3	270	273
10	1	193	198
10	0	92	86
10	-1	108	90
10	-3	332	329
10	-5	174	171
10	-7	121	128
10	-8	78	83
10	-9	188	188
10	-11	94	92
9	-15	125	108
9	-13	87	81
9	-9	58	61
9	-7	117	115
9	-6	131	122
9	-5	154	149
9	-2	67	51
9	-1	178	176
9	0	61	81
9	1	271	276
9	4	125	118
9	5	154	154
9	6	111	112
9	7	136	148
9	9	93	83
9	10	70	64
9	12	81	83
9	13	112	101
8	13	62	2*
8	12	101	105
8	10	97	83
8	9	119	109
8	8	173	172
8	7	212	214
8	6	153	156
8	4	56	68
8	3	410	419
8	1	406	417
8	-1	135	137
8	-2	59	68
8	-3	488	476
8	-5	413	413
8	-6	91	80
8	-7	60	36
8	-8	81	88
8	-9	361	347
8	-11	181	190
8	-14	93	67
8	-15	128	128
7	-15	93	97
7	-13	87	66
7	-12	80	75
7	-11	81	77
7	-10	137	124
7	-9	179	172
7	-7	324	317
7	-6	53	63
7	-5	99	99
7	-4	87	89
7	-3	116	117
7	-2	193	196
7	-1	330	339
7	1	286	287
7	2	114	111
7	3	175	173
7	4	189	189
7	5	146	148
7	7	395	399
7	8	91	85
7	9	182	183
7	10	117	113
7	11	62	67
7	12	102	107
7	13	170	165
7	15	95	95
6	14	99	101
6	13	110	101
6	12	130	137
6	11	89	87
6	10	72	64
6	8	123	129
6	7	140	142
6	6	220	222
6	4	56	43
6	3	296	294
6	2	427	422
6	1	623	628
6	0	157	160
6	-1	258	254
6	-3	675	665
6	-4	233	230
6	-5	647	626
6	-6	134	134
6	-7	81	79
6	-8	129	126
6	-9	459	449
6	-10	103	96
6	-11	382	374
6	-12	62	46
6	-15	158	164
6	-16	102	93
6	-17	134	154
5	-15	103	102
5	-13	136	126
5	-12	80	80
5	-10	173	165
5	-9	72	73
5	-8	59	28*
5	-7	229	224
5	-6	109	115
5	-5	559	557
5	-4	432	428
5	-2	169	172
5	-1	604	610
5	0	238	226
5	1	540	540
5	2	84	64
5	4	521	528
5	5	442	446
5	6	262	267
5	7	268	274
5	9	211	207
5	10	243	248
5	11	59	36
5	12	66	68
5	13	228	227
5	15	166	165
4	17	162	150
4	15	148	128
4	14	89	86
4	13	234	226
4	12	199	189
4	11	92	92
4	10	99	97
4	9	91	90
4	8	471	460
4	6	369	359
4	5	131	133
4	4	75	72
4	3	326	329
4	2	619	599
4	1	322	335
4	0	452	446
4	-1	168	161
4	-2	171	164
4	-3	453	455
4	-4	215	206
4	-5	840	828
4	-6	214	219
4	-7	215	208
4	-8	146	146
4	-9	425	416
4	-11	611	605
4	-13	149	142
4	-15	247	247
4	-17	182	196
3	-16	60	49
3	-15	95	88
3	-13	192	184
3	-12	78	81
3	-11	91	85
3	-9	207	197
3	-8	190	191
3	-7	558	559
3	-6	294	284
3	-5	254	263
3	-4	171	173
3	-3	87	78
3	-2	329	325
3	-1	250	257
3	0	243	234
3	1	839	846
3	2	620	621
3	3	411	390
3	4	271	262
3	5	141	149
3	6	72	64
3	7	622	617
3	8	54	75
3	9	295	295
3	10	290	296
3	11	146	156
3	12	108	115
3	13	173	174
3	15	120	122
3	16	95	78
3	18	72	71
3	19	67	50
2	19	186	174
2	17	192	184
2	15	72	64
2	14	110	110
2	13	413	398
2	12	162	158
2	11	280	278
2	10	119	127
2	9	90	74
2	8	320	317
2	7	495	487
2	6	196	195
2	5	253	258
2	4	70	65
2	3	300	284
2	2	498	485
2	1	376	378
2	0	376	381
2	-1	365	374
2	-2	529	533
2	-3	89	91
2	-4	319	314
2	-5	756	768
2	-6	475	456
2	-7	523	506
2	-9	251	251
2	-10	115	110
2	-11	509	498
2	-12	117	125
2	-13	259	262
2	-15	138	133
2	-17	255	266
2	-18	72	53
2	-19	82	95
1	-15	70	72
1	-13	156	143
1	-12	135	128
1	-11	169	172
1	-10	101	99
1	-9	91	90
1	-8	245	244
1	-7	423	432
1	-6	174	157
1	-5	487	487
1	-4	238	244
1	-3	128	116
1	2	158	147
1	4	170	172
1	5	325	332
1	6	316	298
1	7	439	446
1	8	117	126
1	9	265	265
1	10	76	80
1	13	249	246
1	15	152	155
1	16	67	81
0	19	184	173
0	17	274	267
0	15	69	59
0	14	59	25*
0	13	407	391
0	11	526	508
0	10	116	114
0	9	78	64
0	8	131	130
0	7	495	478
0	6	388	362
0	5	287	284
0	4	172	126
0	3	325	321
K=	3		
12	3	73	32*
12	-1	85	87
12	-7	124	114
11	-11	107	85
11	-9	130	120
11	-5	143	143
11	-3	179	171
11	1	100	106
11	3	124	119
11	5	108	123
11	8	68	57
11	9	69	90
10	9	222	226
10	7	143	145
10	3	106	121
10	-7	75	80
10	-8	87	60
10	-9	150	148
10	-10	77	40*
10	-13	138	107
9	-13	76	71
9	-11	174	153
9	-10	60	28*
9	-9	118	112
9	-5	105	109
9	-4	101	91
9	-3	221	217
9	-2	114	113
9	-1	205	205
9	1	84	62
9	2	90	95
9	3	242	243
9	5	122	134
9	9	94	79
9	11	137	125
9	13	91	78
8	13	165	167
8	10	75	55
8	9	260	257
8	7	310	309
8	4	73	52
8	3	364	363
8	1	314	316
8	0	105	110
8	-3	132	137
8	-4	94	89
8	-7	74	72
8	-8	58	51
8	-9	145	128
8	-10	73	60
8	-11	114	104
8	-13	66	40
8	-14	67	53
8	-15	156	145
7	-15	85	64
7	-13	62	29*
7	-11	189	173
7	-9	249	247
7	-7	127	111
7	-5	292	296
7	-4	88	82
7	-3	220	220
7	-2	113	108
7	-1	57	53
7	2	157	174
7	3	166	173
7	4	175	170
7	5	414	421
7	7	131	123
7	8	188	189
7	9	190	199
7	11	192	203
7	13	83	64
6	15	130	140
6	13	351	345
6	11	114	95
6	9	443	443
6	7	553	558
6	6	92	70
6	5	82	66
6	4	191	195
6	3	435	442
6	2	74	68
6	1	342	341
6	0	135	150
6	-1	140	145
6	-2	111	104
6	-3	213	207
6	-5	191	190
6	-6	117	104
6	-7	91	76
6	-8	100	99
6	-11	63	68
6	-15	155	132
6	-16	75	55
6	-17	114	118
5	-17	176	148
5	-13	127	106
5	-12	113	108
5	-11	260	246
5	-10	103	100
5	-9	100	85
5	-8	145	138
5	-7	105	103
5	-6	93	105
5	-5	83	76
5	-4	151	169
5	-3	521	523
5	-2	232	238
5	-1	233	237
5	0	192	192
5	1	265	257
5	2	151	152
5	3	479	488
5	4	61	57
5	5	108	110
5	9	117	111
5	10	57	43
5	11	261	257
5	13	137	125
5	14	72	92
5	17	140	127
4	17	74	71
4	15	135	122
4	13	307	298
4	11	266	271
4	10	195	203
4	9	228	228
4	8	62	58
4	7	634	627
4	6	115	110
4	5	520	513
4	4	156	164
4	3	503	499
4	2	110	112
4	1	1051	1050
4	0	101	105
4	-1	119	118
4	-2	63	63
4	-3	414	400
4	-4	189	188
4	-5	446	432
4	-6	189	190
4	-7	93	96
4	-8	81	73
4	-10	173	167
4	-12	81	74
4	-16	69	74
4	-17	120	118
3	-17	135	125
3	-15	82	82
3	-14	92	77
3	-13	156	145
3	-11	353	346
3	-9	277	274
3	-8	164	160
3	-7	163	157
3	-5	598	603
3	-4	88	83
3	-3	299	297
3	-2	113	107
3	-1	277	276
3	1	56	43
3	2	230	229
3	3	609	605
3	4	197	193
3	5	562	558
3	6	307	308
3	7	67	57
3	9	384	379
3	10	95	90
3	11	207	196
3	16	103	97
3	17	134	120
2	17	92	83
2	13	271	257
2	12	107	93
2	11	391	384
2	9	164	156
2	8	88	76
2	7	983	981
2	5	741	734
2	4	131	122
2	3	230	232
2	2	74	87
2	1	1231	1257
2	0	505	498
2	-1	1070	1096
2	-2	139	140
2	-3	134	135
2	-4	305	284
2	-5	792	790

Table 2. Continued.

H	L		
K= 3			
2	-6	242	227
2	-7	439	439
2	-8	151	155
2	-9	181	172
2	-10	73	76
2	-11	161	152
2	-17	77	71
2	-18	70	50
1	-19	126	118
1	-17	189	175
1	-13	131	126
1	-12	66	48
1	-11	253	246
1	-10	116	109
1	-9	297	296
1	-8	77	75
1	-7	114	109
1	-6	137	130
1	-5	468	454
1	-4	234	229
1	-3	876	869
1	3	681	669
1	4	401	382
1	5	381	387
1	6	279	271
1	8	58	63
1	9	323	316
1	11	381	375
1	12	178	175
1	13	194	189
1	15	86	90
1	17	143	144
1	19	114	111
0	18	84	81
0	16	83	61
0	13	257	244
0	12	118	109
0	11	331	318
0	10	114	120
0	8	62	74
0	7	654	638
0	6	113	87
0	5	1038	1004
0	3	168	161
0	2	42	39
K= 4			
12	5	119	108
12	3	176	182
12	-1	124	115
12	-3	160	149
12	-5	69	58
11	-10	66	51
11	-8	64	61
11	-7	115	120
11	-5	92	93
11	-4	110	122
11	-2	72	57
11	-1	165	160
11	1	129	141
11	2	99	90
11	4	66	91
11	5	124	106
11	7	126	140
10	11	95	91
10	10	90	92
10	9	136	146
10	8	127	125
10	5	95	117
10	3	192	196
10	1	112	124
10	-1	99	106
10	-3	210	218
10	-5	124	110
10	-7	81	81
10	-9	146	152
10	-13	63	17*
9	-13	89	82
9	-10	123	123
9	-9	63	48
9	-8	83	68
9	-7	157	147
9	-5	191	180
9	-4	153	142
9	-3	66	59
9	-2	122	120
9	-1	209	213
9	1	226	231
9	2	122	123
9	4	62	65
9	5	137	131
9	6	68	14*
9	7	99	107
9	10	83	50
9	13	87	73
8	12	84	71
8	10	84	77
8	9	76	45
8	8	199	197
8	7	110	114
8	6	94	91
8	5	86	94
8	4	121	119
8	3	291	296
8	2	251	255
8	1	177	187
8	-1	164	182
8	-2	85	101
8	-3	369	362
8	-4	64	47
8	-5	205	199
8	-7	67	70
8	-9	228	220
8	-10	130	133
8	-11	109	107
8	-14	80	62
7	-14	75	64
7	-13	71	84
7	-12	104	114
7	-11	107	88
7	-10	135	138
7	-9	116	120
7	-8	82	82
7	-7	268	268
7	-6	179	176
7	-5	91	94
7	-4	264	259
7	-3	155	160
7	-1	225	232

H	L		
7	1	128	136
7	2	161	170
7	3	110	120
7	4	140	156
7	5	98	84
7	6	58	80
7	7	185	196
7	9	102	110
7	10	85	91
7	13	72	51
6	14	173	176
6	13	67	54
6	12	157	154
6	11	84	91
6	9	67	45
6	8	397	405
6	6	190	202
6	4	106	102
6	3	166	165
6	2	264	273
6	1	308	316
6	0	222	223
6	-1	126	134
6	-2	96	96
6	-3	333	335
6	-5	303	304
6	-6	98	96
6	-9	232	225
6	-11	179	170
6	-12	101	91
6	-15	79	89
6	-17	90	92
5	-16	162	147
5	-15	112	112
5	-13	127	125
5	-12	113	110
5	-10	165	159
5	-9	135	130
5	-8	165	150
5	-7	168	153
5	-6	167	161
5	-5	216	220
5	-4	124	131
5	-3	95	91
5	-2	230	235
5	-1	340	345
5	0	117	123
5	1	143	145
5	2	270	262
5	3	197	201
5	5	202	203
5	6	79	79
5	8	94	88
5	9	80	76
5	10	63	62
5	12	116	115
5	13	81	85
5	14	73	67
5	15	121	122
4	17	120	104
4	14	170	163
4	13	120	114
4	12	184	180
4	10	78	71
4	8	270	265
4	6	489	489
4	5	136	136
4	4	116	122
4	3	138	132
4	2	423	428
4	1	197	203
4	0	515	512
4	-1	157	158
4	-2	221	208
4	-3	208	215
4	-4	495	486
4	-5	493	488
4	-6	63	66
4	-7	206	205
4	-9	255	254
4	-10	87	91
4	-11	407	404
4	-12	56	31*
4	-13	76	76
4	-15	113	107
4	-16	90	81
4	-17	124	111
3	-18	76	81
3	-16	92	101
3	-15	116	111
3	-13	186	189
3	-12	155	154
3	-10	294	300
3	-9	347	346
3	-8	49	38
3	-7	436	435
3	-6	222	228
3	-5	43	25
3	-4	243	238
3	-3	437	430
3	-2	271	276
3	-1	214	220
3	1	194	201
3	3	100	96
3	4	324	321
3	5	91	87
3	6	168	156
3	7	215	212
3	8	53	29*
3	9	142	135
3	11	64	36*
3	12	153	155
3	13	91	72
3	15	93	104
3	18	84	83
2	17	115	115
2	14	57	54
2	13	197	197
2	12	250	253
2	11	165	171
2	9	54	53
2	8	283	282
2	7	155	150
2	6	558	563
2	5	91	114
2	4	96	94
2	3	186	191
2	2	579	582
2	1	437	436
2	0	530	542
2	-1	262	259
2	-2	322	329
2	-3	269	284

H	L		
2	-4	416	408
2	-5	626	631
2	-6	328	333
2	-7	281	271
2	-9	119	117
2	-10	153	149
2	-11	325	328
2	-12	75	80
2	-13	200	202
2	-14	95	84
2	-15	91	81
2	-17	164	160
2	-19	91	81
1	-19	74	57
1	-18	114	120
1	-16	110	96
1	-15	171	158
1	-13	197	194
1	-12	144	139
1	-10	144	141
1	-9	218	204
1	-7	363	363
1	-6	77	74
1	-5	87	97
1	-4	266	267
1	-3	286	286
1	2	183	187
1	3	145	135
1	4	223	231
1	5	179	189
1	6	89	81
1	7	340	346
1	8	68	63
1	9	261	259
1	10	193	194
1	12	206	209
1	13	193	190
1	14	69	57
1	15	177	180
1	18	126	126
1	19	74	40*
0	19	111	103
0	17	182	177
0	15	102	97
0	13	234	226
0	12	182	180
0	11	387	376
0	10	199	192
0	9	161	161
0	8	67	60
0	7	249	237
0	6	494	477
0	5	315	317
0	4	502	491
0	2	295	292
K= 5			
12	4	164	157
12	2	90	84
12	-2	124	127
12	-4	116	105
11	-6	80	75
11	-5	65	37*
11	0	81	95
11	2	90	95
11	6	78	79
11	8	80	95
10	-10	63	86
10	-8	153	139
10	-7	69	82
10	-4	207	201
10	-2	180	184
10	2	232	227
10	4	154	146
10	7	82	81
10	8	108	104
10	10	69	77
9	11	103	81
9	8	98	101
9	6	125	115
9	5	77	83
9	4	64	52
9	2	77	88
9	0	154	155
9	-2	100	92
9	-4	61	44
9	-6	135	120
9	-8	104	94
9	-12	64	43
9	-14	98	73
8	-15	68	43
8	-14	79	72
8	-12	89	88
8	-10	240	216
8	-9	75	66
8	-8	155	147
8	-6	115	112
8	-4	363	359
8	-2	225	220
8	-1	116	111
8	0	105	104
8	1	82	69
8	2	313	319
8	4	167	163
8	6	91	85
8	8	123	132
8	9	60	42
7	14	85	99
7	12	72	81
7	11	128	123
7	8	191	191
7	7	65	59
7	6	180	189
7	5	205	201
7	4	103	98
7	3	126	127
7	2	180	185
7	1	90	88
7	0	291	298
7	-1	87	76
7	-2	170	163
7	-3	55	23*
7	-6	234	223
7	-7	70	51
7	-8	149	145
7	-10	72	58
7	-12	67	55
7	-14	111	94
6	-16	153	132
6	-15	65	51
6	-14	110	96
6	-12	147	133

H	L		
6	-10	325	304
6	-9	76	53
6	-8	256	242
6	-6	339	328
6	-4	516	507
6	-2	174	167
6	0	276	281
6	1	81	88
6	2	428	429
6	3	102	89
6	5	92	88
6	6	57	57
6	7	143	138
6	8	82	79
6	9	105	103
6	14	91	85
5	16	81	64
5	14	185	179
5	12	76	85
5	11	110	118
5	9	164	171
5	8	254	247
5	6	274	266
5	5	148	149
5	4	57	51
5	3	180	180
5	2	126	131
5	0	429	433
5	-1	161	160
5	-2	166	164
5	-3	92	96
5	-4	85	95
5	-5	97	92
5	-6	286	277
5	-7	101	93
5	-8	231	218
5	-10	55	53
5	-12	58	63
5	-14	144	128
5	-16	73	60
4	-16	240	210
4	-15	69	46
4	-12	245	226
4	-10	429	411
4	-9	81	79
4	-8	99	101
4	-7	104	98
4	-6	359	350
4	-5	135	131
4	-4	373	369
4	-2	249	252
4	-1	55	57
4	0	270	266
4	1	90	89
4	2	208	201
4	3	107	102
4	4	62	67
4	7	108	108
4	9	89	75
4	12	163	160
4	13	89	72
4	14	131	125
4	18	125	121
3	15	74	74
3	14	149	150
3	13	73	49
3	12	109	100
3	11	102	99
3	10	125	113
3	9	157	157
3	8	228	224
3	6	308	312
3	5	216	220
3	4	86	82
3	3	277	275
3	2	307	301
3	0	387	386
3	-1	236	231
3	-2	232	237
3	-3	283	282
3	-4	212	222
3	-6	262	257
3	-7	127	117
3	-8	283	277
3	-10	50	14*
3	-12	146	142
3	-14	117	89
2	-18	148	133
2	-16	174	158
2	-12	294	281
2	-11	79	80
2	-10	368	362
2	-8	93	94
2	-6	416	405
2	-5	145	140
2	-4	346	344
2	-2	108	101
2	-1	236	237
2	0	210	208
2	1	393	397
2	2	108	95
2	4	78	80
2	5	197	207
2	6	221	214
2	7	131	137
2	8	258	254
2	9	79	72
2	10	81	85
2	12	336	316
2	14	140	137
2	15	61	55
2	16	65	47
2	18	176	161
1	16	81	73
1	14	135	135
1	12	136	132
1	10	134	118
1	9	247	243
1	8	258	252
1	7	157	156
1	6	247	240
1	5	155	146
1	4	67	64
1	3	459	459
1	2	255	262
1	-3	158	154
1	-4	75	82
1	-5	93	105
1	-6	247	245
1	-7	153	143
1	-8	194	176
1	-9	118	125
1	-12	125	120

H			
1	-13	56	43
1	-14	98	90
1	-15	70	52
1	-16	66	54
0	2	135	131
0	4	52	59
0	6	238	232
0	7	253	255
0	8	200	202
0	10	179	167
0	11	99	98
0	12	329	315
0	13	88	76
0	14	130	126
0	16	141	133
0	18	196	188
K= 6			
12	-2	75	66
11	-10	71	60
11	-4	95	88
11	4	76	84
11	6	65	60
10	10	66	89
10	8	109	101
10	3	85	81
10	2	64	57
10	-3	123	134
10	-7	61	56
10	-8	85	72
10	-10	81	73
9	-12	71	79
9	-10	78	89
9	-6	63	67
9	-4	101	100
9	0	70	33*
9	1	95	96
9	2	76	65
9	3	79	71
9	4	111	121
9	6	81	79
9	8	74	19*
9	9	69	75
9	10	109	109
9	12	90	81
8	14	116	115
8	12	93	80
8	10	85	75
8	8	218	217
8	6	94	97
8	5	58	17*
8	4	104	100
8	2	180	176
8	0	57	53
8	-5	67	67
8	-8	83	89
8	-9	83	78
8	-10	89	102
8	-11	60	32*
8	-14	85	99
7	-12	96	102
7	-10	78	84
7	-9	66	63
7	-8	60	44
7	-7	58	25*
7	-4	147	141
7	-3	107	106
7	-2	155	159
7	-1	90	88
7	0	85	76
7	2	137	141
7	3	90	96
7	4	207	208
7	5	83	73
7	6	140	149
7	7	112	99
7	10	182	170
7	12	92	91
6	14	183	176
6	12	127	134
6	10	68	76
6	8	324	324
6	6	209	212
6	5	74	62
6	4	79	89
6	3	91	98
6	2	257	263
6	1	73	73
6	0	232	231
6	-3	102	101
6	-4	87	85
6	-5	70	79
6	-6	81	87
6	-8	61	47
6	-9	58	70
5	-17	65	22*
5	-16	95	79
5	-13	72	38*
5	-12	103	93
5	-11	54	54
5	-10	114	117
5	-8	102	97
5	-7	66	66
5	-6	49	61
5	-4	137	140
5	-3	91	90
5	-2	266	262
5	0	92	87
5	1	115	117
5	2	194	191
5	3	101	89
5	4	299	298
5	6	194	192
5	7	64	62
5	8	127	126
5	9	61	65
5	10	209	207
5	12	147	138
5	13	75	63
5	16	108	92
4	14	170	163
4	13	68	66
4	12	188	178
4	9	76	77
4	8	322	313
4	6	424	427
4	5	.74	85
4	3	81	63
4	2	448	442
4	1	112	116
4	0	426	423
4	-1	73	62

H	L		
4	-2	80	74
4	-3	70	62
4	-4	304	316
4	-5	79	84
4	-6	120	131
4	-7	106	118
4	-11	74	71
4	-16	80	84
3	-16	74	61
3	-12	78	64
3	-11	58	53
3	-10	165	176
3	-9	74	72
3	-8	119	117
3	-4	236	236
3	-3	100	98
3	-2	408	407
3	0	105	101
3	1	136	147
3	2	229	227
3	4	434	431
3	5	193	197
3	6	153	161
3	7	178	182
3	8	160	159
3	9	58	66
3	10	190	193
3	11	110	107
3	12	138	128
3	16	79	63
3	18	68	73
2	14	107	107
2	12	218	216
2	8	309	305
2	6	474	478
2	4	59	44
2	3	210	206
2	2	441	444
2	0	475	487
2	-1	200	203
2	-2	171	171
2	-4	320	328
2	-5	151	146
2	-6	308	307
2	-7	125	142
2	-8	92	86
2	-9	123	140
2	-10	98	102
2	-11	93	100
2	-12	89	87
2	-17	72	75
1	-18	89	87
1	-16	61	53
1	-12	74	77
1	-11	85	79
1	-10	161	163
1	-8	120	128
1	-7	82	89
1	-5	301	307
1	-4	329	336
1	-2	359	362
1	2	307	307
1	4	421	412
1	5	127	122
1	6	104	90
1	7	81	82
1	8	146	147
1	10	234	223
1	11	109	99
1	12	120	121
1	13	68	84
1	15	80	66
1	16	63	56
1	18	98	76
0	17	61	64
0	14	72	48
0	13	88	83
0	12	151	142
0	11	101	112
0	10	88	92
0	9	113	117
0	8	117	99
0	7	71	73
0	6	436	424
0	4	363	354
0	3	163	163
0	2	298	305
K= 7			
10	10	66	64
10	9	107	94
10	8	62	47
10	4	105	117
10	3	65	55
10	2	132	124
10	-1	66	41
10	-2	122	117
10	-4	104	109
10	-8	66	50
9	-6	135	142
9	-5	69	64
9	-3	93	97
9	-2	89	95
9	0	134	132
9	3	137	132
9	4	76	81
9	6	79	79
8	9	110	119
8	8	63	58
8	7	120	132
8	4	92	101
8	3	100	110
8	2	115	137
8	1	97	97
8	-1	53	61
8	-2	109	113
8	-4	137	140
8	-8	92	101
8	-10	61	80
7	-14	70	67
7	-12	68	55
7	-11	71	70
7	-9	102	104
7	-8	107	120
7	-6	157	151
7	-5	89	86
7	-3	74	68
7	-2	133	133
7	-1	63	49
7	0	171	179
7	4	71	84
7	6	68	62

H	L		
7	9	62	65
7	15	61	5*
6	13	103	105
6	9	112	114
6	7	150	166
6	3	163	166
6	2	141	151
6	1	132	136
6	0	102	106
6	-2	112	116
6	-3	106	108
6	-4	185	194
6	-5	67	77
6	-6	91	95
6	-8	73	81
6	-10	108	122
5	-14	79	101
5	-12	87	87
5	-11	76	96
5	-10	70	50
5	-9	73	59
5	-8	186	194
5	-6	131	127
5	-5	119	130
5	-4	95	89
5	-3	130	137
5	-2	183	195
5	0	94	95
5	1	83	79
5	2	48	63
5	3	92	81
5	5	56	70
5	10	56	42
4	13	103	109
4	12	82	67
4	9	98	90
4	8	52	20*
4	7	227	233
4	5	148	162
4	4	48	39
4	3	103	105
4	2	138	153
4	1	289	290
4	0	109	123
4	-1	112	113
4	-2	60	61
4	-3	121	116
4	-4	163	180
4	-5	74	87
4	-6	157	164
4	-10	126	148
4	-12	82	103
3	-14	105	120
3	-12	65	66
3	-11	98	108
3	-10	58	81
3	-9	96	98
3	-8	240	250
3	-7	61	78
3	-6	92	100
3	-5	100	109
3	-4	120	112
3	-3	54	53
3	-2	198	202
3	0	98	104
3	1	102	101
3	2	70	58
3	3	137	134
3	5	84	90
3	7	56	53
3	9	87	86
3	10	68	70
3	13	58	58
3	16	63	77
2	13	129	126
2	12	97	115
2	11	145	155
2	10	75	77
2	7	280	281
2	6	84	89
2	5	218	212
2	4	74	69
2	3	113	111
2	1	225	236
2	0	157	160
2	-1	213	223
2	-3	81	89
2	-4	193	204
2	-5	206	210
2	-6	220	230
2	-7	161	164
2	-10	196	205
2	-11	102	115
2	-12	117	120
1	-18	64	26*
1	-17	78	89
1	-16	61	89
1	-14	105	128
1	-11	127	139
1	-10	157	161
1	-9	103	106
1	-8	204	206
1	-6	71	51
1	-5	139	144
1	-4	57	72
1	-3	281	278
1	-2	191	201
1	3	100	97
1	4	79	65
1	5	117	121
1	6	69	70
1	8	131	138
1	9	52	31
1	10	116	129
1	11	133	131
1	14	110	120
1	15	63	36*
1	16	65	69
1	17	69	62
0	16	71	60
0	13	56	55
0	12	160	163
0	11	89	88
0	10	115	124
0	8	51	52
0	7	139	146
0	6	88	83
0	5	358	354
0	4	153	162
0	2	68	76

Table 2. Continued.

H	L			H	L			H	L			H	L			H	L			H	L		
K=	8			8	8	59	45	6	3	129	129	4	-9	144	141	3	-2	159	168	2	6	88	93	1	-9	131	136
				8	9	77	75	6	9	57	37	4	-7	71	67	3	-6	64	64	2	7	52	60	1	-10	60	61
				7	13	67	54	5	14	63	41	4	-5	225	235	3	-7	131	143	2	11	113	116	1	-13	76	76
9	7	77	77	7	7	95	87	5	13	65	53	4	-3	158	167	3	-8	56	56	2	13	105	104	1	-15	72	78
9	6	73	64	7	6	89	73	5	10	91	92	4	-1	48	58	3	-9	89	90	2	17	74	75	0	2	91	97
9	5	67	76	7	5	91	80	5	9	76	67	4	1	170	181	3	-12	66	30*	1	15	65	68	0	3	48	51
9	4	58	29*	7	1	119	116	5	7	110	116	4	3	70	75	3	-13	100	95	1	13	85	86	0	4	61	55
9	1	101	109	7	0	92	91	5	6	103	97	4	11	85	67	2	-17	80	98	1	10	78	67	0	5	135	134
9	0	59	41	7	-1	121	122	5	5	63	60	4	13	96	93	2	-15	56	58	1	9	104	111	0	6	89	87
9	-1	111	111	7	-2	61	62	5	4	117	117	3	15	72	79	2	-13	86	81	1	8	160	156	0	7	142	139
9	-5	71	75	7	-4	56	67	5	1	124	131	3	13	91	88	2	-11	191	192	1	7	82	89	0	11	157	162
9	-7	89	68	7	-5	91	82	5	0	60	80	3	10	89	69	2	-9	121	125	1	4	215	218	0	13	94	104
9	-13	62	44	7	-7	136	133	5	-1	169	186	3	9	88	87	2	-8	83	81	1	3	86	89	0	17	104	95
8	-11	76	75	7	-13	71	76	5	-3	82	77	3	8	105	101	2	-7	115	125	1	2	124	137				
8	-9	100	102	7	-14	70	45	5	-5	77	90	3	7	123	126	2	-5	170	170	1	-2	179	193				
8	-8	67	24*	6	-14	60	18*	5	-7	175	183	3	5	69	75	2	-3	73	74	1	-3	68	67				
8	-7	61	41	6	-11	118	127	5	-9	70	80	3	4	117	122	2	-2	55	54	1	-4	120	123				
8	-5	128	127	6	-9	155	163	5	-13	57	69	3	2	143	146	2	-1	59	58	1	-5	79	80				
8	-3	155	158	6	-5	195	206	4	-17	74	74	3	1	106	101	2	0	82	85	1	-6	57	54				
8	1	132	132	6	-3	189	192	4	-11	149	153	3	0	54	43	2	1	39	40	1	-7	147	162				
8	3	138	156	6	1	143	152	4	-10	55	23*	3	-1	160	161	2	5	76	54	1	-8	66	60				

than the 2.488 Å separation in the tetrahydrate, while the Mn – O distances in both the compounds are of about the same order of magnitude. It seems that the exchange from water to glycol has had some effect on the Mn – Cl bond. In both structures the chlorine atoms are adjacent to each other and participate in hydrogen bonds to oxygen atoms in neighbouring octahedra. Evidently the exchange from water to glycol increases the distortion of the octahedral arrangement around the manganese atom. In $MnCl_2.4H_2O$ the angles between opposite corners *via* the central atom are very near 180°. One angle differs from this value by 11° and the other two by 6° and 3°, respectively. In $[MnCl_2(C_2H_6O_2)_2]$ none of these angles differs by less than 16° and by more than 22°.

Comparisons can also be made with the dihydrate of $MnCl_2$.[11] This compound consists of polymeric chains of metal and chlorine ions arranged in a near square planar configuration with each chlorine ion shared by two metal ions. The water molecules which fill the remaining octahedral positions around the metal ion also link adjacent chains through hydrogen bonding. In this compound the Mn – Cl distances of 2.515 Å and 2.592 Å are significantly longer than in the glycol compound while the Mn – O distance of 2.150 Å is significantly shorter than the Mn – O distances in the glycol compound. There seems to be a tendency for the Mn – Cl distance to decrease in the series $MnCl_2.2H_2O \rightarrow MnCl_2.4H_2O \rightarrow [MnCl_2(C_2H_6O_2)_2]$ and at the same time the Mn – O distances increase. In the same series the Cl – Cl distances within the coordination octahedra vary from 3.530 Å and 3.691 Å for $MnCl_2.2H_2O$ to 3.708 Å for the tetrahydrate and 3.717 Å for $[MnCl_2(C_2H_6O_2)_2]$. The angles Cl – Mn – Cl show the same trend; they are 87°, 96°, and 98° respectively.

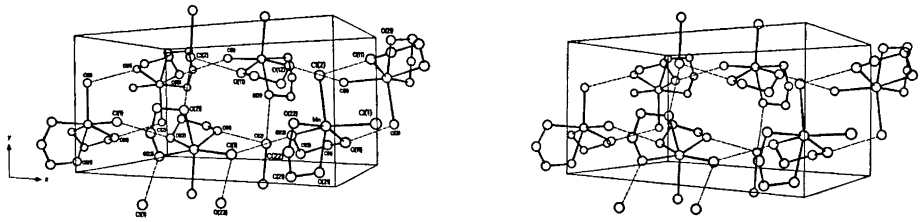

Fig. 1. A stereoscopic illustration of the molecular packing and the hydrogen bond contacts in a unit cell of $[MnCl_2(C_2H_6O_2)_2]$.

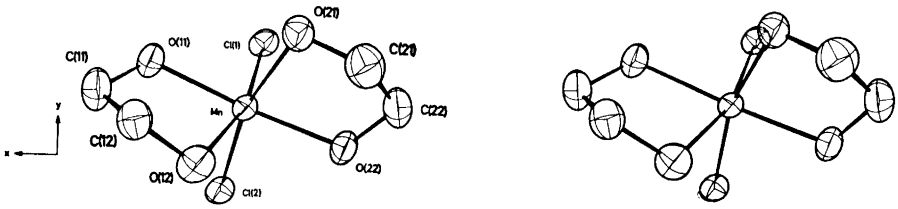

Fig. 2. A stereoscopic view of the atoms in the asymmetric unit, showing the coordination around manganese. Thermal ellipsoids are scaled to enclose 50 % probability.

The greatest differences in angles and distances occur between $MnCl_2.2H_2O$ on the one hand and $MnCl_2.4H_2O$ and $[MnCl_2(C_2H_6O_2)_2]$ on the other. It is also between the two $MnCl_2$-hydrates that a structural change occurs from polymeric chains to discrete octahedra, the latter being retained in $[MnCl_2(C_2H_6O_2)_2]$.

The glycol molecules act as bidentate ligands coordinating to the manganese atom through the two *vicinal* hydroxyl groups. As can be seen from Fig. 2 the glycol molecules do not expand in the same plane but are twisted in relation to each other. This is a natural consequence of the *cis*-configuration of the molecule. The angles between connected planes [1] in the two glycol ligands are nearly the same, 52.3° and 52.1° for Glycol I and II, respectively. The equations for these planes are given in Table 4. In the structure $[Cu(C_2H_6O_2)_3]SO_4$ these angles varied between 45.9° to 55.3° for the three glycol ligands.[1] When the glycol molecule is unstrained the carbon-carbon bond is twisted in such a way

Table 3. Dimensions of the octahedron around manganese in $[MnCl_2(C_2H_6O_2)_2]$. (Standard deviations for the last significant figure are given in parentheses.)

Atoms	Distance, Å.	Atoms	Angle(°)	Atoms	Angle(°)
Mn–Cl(1)	2.463(1)	Cl(1)–Mn–Cl(2)	98.0(0.4)	O(11)–Mn–O(21)	89.3(1)
Mn–Cl(2)	2.464(1)	Cl(1)–Mn–O(11)	91.6(1)	O(11)–Mn–O(22)	157.7(1)
Mn–O(11)	2.184(3)	Cl(1)–Mn–O(21)	90.9(1)	O(11)–Mn–O(12)	72.4(1)
Mn–O(12)	2.247(3)	Cl(1)–Mn–O(22)	101.8(1)	O(21)–Mn–O(22)	72.9(1)
Mn–O(21)	2.233(3)	Cl(1)–Mn–O(12)	163.7(1)	O(21)–Mn–O(12)	85.6(1)
Mn–O(22)	2.197(3)	Cl(2)–Mn–O(11)	104.7(1)	O(22)–Mn–O(12)	92.4(1)
		Cl(2)–Mn–O(21)	163.1(1)		
		Cl(2)–Mn–O(22)	91.1(1)		
		Cl(2)–Mn–O(12)	89.6(1)		

Table 4. The equations for the planes 1–4 in the glycol ligands. The numbering of the planes is the same as in Table 5.

1: $0.584587x - 0.523141y - 0.620146z - 1.627167 = 0$
2: $-0.093764x - 0.959094y - 0.267110z - 4.092643 = 0$
3: $0.549048x - 0.521635y - 0.653027z - 4.908709 = 0$
4: $-0.116435x - 0.060177y - 0.991374z - 5.225780 = 0$

Table 5. Dimensions of the two glycol ligands I and II. (Standard deviations of the last significant figure are given in parentheses.)

Atoms	Distance, Å	Plane	Atoms	Angle(°)
		I		
O(11)–C(11)	1.442(6)	1	O(11)–C(11)–C(12)	107.0(3)
O(12)–C(12)	1.439(6)	2	O(12)–C(12)–C(11)	106.5(4)
C(11)–C(12)	1.490(7)	1–2		52.3
		II		
O(21)–C(21)	1.425(6)	3	O(21)–C(21)–C(22)	107.3(4)
O(22)–C(22)	1.444(6)	4	O(22)–C(22)–C(21)	107.4(4)
C(21)–C(22)	1.486(8)	3–4		52.1

Table 6. Hydrogen bond distances and their estimated standard deviations. (All distances represent hydrogen bonding between atoms in different octahedra).

Bond	Distance, Å
O(11)–H···Cl(2)	3.112(3)
O(12)–H···Cl(1)	3.116(3)
O(21)–H···Cl(2)	3.108(3)
O(22)–H···Cl(1)	3.109(3)

as to achieve a *staggered* conformation and this angle is approximately 55°. In $[MnCl_2(C_2H_6O_2)_2]$ the glycol molecules are evidently somewhat strained in order to achieve a molecular packing with lowest possible energy. This fact is also reflected in the O–C–C angles in the glycol ligands, which deviate significantly from the tetrahedral angle of 109.5°. The mean values of the O–C–C angles for Glycol I is 106.8° and for Glycol II 107.4°. With regard to the interatomic distances within the glycol ligands, there are no significant deviations from earlier reported values.[1] A complete list of bond distances and angles in the two glycol ligands is presented in Table 5.

As mentioned earlier the whole structure is held together by weak hydrogen bonds and van der Waals contacts. Each oxygen atom in the two glycol ligands is involved in a hydrogen bond to a chlorine atom in a neighbouring molecule. The hydrogen bond distances are listed in Table 6.

The O–H distances calculated from the parameters listed in Tables 1a and 1b are 0.92 Å, 0.87 Å, 1.04 Å, and 0.93 Å for O(11), O(12), O(21), and O(22), respectively. The C–H distances are 1.08 Å and 1.00 Å for C(11); 1.02 Å and 0.94 Å for C(12), 1.15 Å and 1.07 Å for C(21), and 1.00 Å and 0.97 Å for C(22). No detailed list of distances and angles concerning the hydrogen atoms is represented because of the limited accuracy of the hydrogen parameters.

In octahedral complexes of the type MeA_4B_2 there are two possible ways of arranging the atoms, which lead to the *cis*- and *trans*-form, respectively.[12]

This also holds true when A_4 represents the four coordinating atoms from two bidentate chelating agents as in $[MnCl_2(C_2H_6O_2)_2]$ the subject of this report. Thus it would appear possible that the *trans*-form of this compound may also be found.

$MnCl_2.4H_2O$ appears in two monoclinic crystal modifications.[13,14] One of them, the α-form, is stable at room temperature and the other, the β-form, is metastable at room temperature. When preparing the $[MnCl_2(C_2H_6O_2)_2]$ crystals the α-form was used. In α-$MnCl_2.4H_2O$ the chlorine atoms are in the *cis*-position as mentioned earlier and the derived compound $[MnCl_2(C_2H_6O_2)_2]$ has retained this *cis*-configuration. β-$MnCl_2.4H_2O$ is isomorphous with $FeCl_2.4H_2O$,[14] the structure of which has been determined by Penfold and Grigor.[15] In this structure the chlorine atoms are in the *trans*-position, an thus should also be so in the isomorphous compound β-$MnCl_2.4H_2O$. It therefore seems possible that the *trans*-form of $[MnCl_2(C_2H_6O_2)_2]$ should arise if the crystals are prepared from β-$MnCl_2.4H_2O$ and glycol. The metastability of β-$MnCl_2.4H_2O$ would serve as an explanation for the failure of the *trans*-compound to form at room temperature.

Acknowledgements. I thank Professor Nils Ingri for his great interest in the present work and for all the facilities placed at my disposal. This work has been financially supported by *Swedish Natural Science Research Council.*

REFERENCES

1. Antti, B.-M., Lundberg, B. K. S. and Ingri, N. *Acta Chem. Scand.* **26** (1972) 3984.
2. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1965, Vol. I.
3. Ivarsson, G., Lundberg, B. K. S. and Ingri, N. *Acta Chem. Scand.* **26** (1972) 3005.
4. Antti, C.-J. and Lundberg, B. K. S. *Acta Chem. Scand.* **25** (1971) 1758.
5. Cruickshank, D. W. J. *Computing Methods in Crystallography*, Pergamon, London 1965, p. 114.
6. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
7. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* **42** (1965) 3175.
8. Hamilton, W. C. *Acta Cryst.* **18** (1965) 502.
9. Pawley, G. S. *Acta Cryst.* **A 26** (1970) 691.
10. Zalkin, A., Forrester, J. D. and Templeton, D. H. *Inorg. Chem.* **3** (1964) 529.
11. Morosin, B. and Graeber, E. J. *J. Chem. Phys.* **42** (1965) 898.
12. Werner, A. *Ber.* **45** (1911) 121.
13. Groth, P. *Chemische Krystallographie*, Wilhelm Engelmann, Leipzig 1908, Vol. I.
14. Dawson, H. M. and Williams, P. *Z. physik. Chem. (Leipzig)* **31** (1899) 59.
15. Penfold, B. R. and Grigor, J. A. *Acta Cryst.* **12** (1959) 850.

Received June 21, 1973.