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The Crystal Structure of Pilocarpine-trichlorogermanate(II) Hemihydrate

SIDSEL FREGERSLEV and SVEND ERIK RASMUSSEN

Department of Inorganic Chemistry, University of Aarhus, 8000 Aarhus C, Denmark

The crystal structure of pilocarpine-trichlorogermanate(II), ($C_{11}H_{17}N_2O_2$,$GeCl_3$,$\frac{1}{2}H_2O$) has been determined using automatically collected counter data and refined to an R-value of 7.8 %. The space group is $P2_1$ (No. 4) with $a = 14.24$ Å, $b = 17.61$ Å, $c = 6.83$ Å, $\beta = 97.25°$. There are four formula units per unit cell. The structure can be described as being composed of pilocarpinium ions and trichlorogermanate(II) ions.

In the compound $CsGeCl_3$ there has been shown [1] to be a pronounced tendency towards the formation of $GeCl_3$ units. There are three short Ge—Cl distances of 2.31 Å and three longer bonds of 3.13 Å. The chlorine atoms lie at the vertices of a distorted octahedron.

The purpose of this investigation was to observe the changes in the anion when the caesium ion was replaced by a large organic ion. Tetraethylammonium trichlorogermanate(II) was prepared but no crystals suitable for a single-crystal X-ray investigation could be prepared. Pilocarpine-trichlorogermanate(II), however, was found to form large well-developed crystals.

This compound was first described by Tchakirian.[2] To our knowledge the crystal structure of pilocarpine itself has not been determined, although the space group of pilocarpine hydrochloride is known.[3]

EXPERIMENTAL

Chemistry. Slow evaporation of a solution formed by dissolving $HGeCl_3$ and pilocarpine hydrochloride in concentrated hydrochloric acid yielded crystals of pilocarpine-trichlorogermanate(II). These crystals were often large and frequently exhibited intergrowth and twinning. The compound was found to crystallize with half a molecule of water per formula unit.

Analysis. Found: Cl 26.66; N 7.12; C 34.16; H 4.56. Calc. for $C_{11}H_{17}N_2O_2$, $GeCl_3$,$\frac{1}{2}H_2O$: Cl 26.85; N 7.07; C 33.34; H 4.32.

X-Ray technique. Unit cell and space group were established from Weissenberg, precession and retigraph films using Cu- and Mo-radiations. A crystal of dimensions $0.4 \times 0.4 \times 2$ mm^3 was sealed in a capillary tube. The crystal was mounted along the needle direction which was the c-axis and intensities were measured with a linear diffractometer designed by Arndt and Phillips [4] and manufactured by Hilger and Watts. Mo-radiation was employed. Balanced filters SrO,ZrO_2 in conjunction with a pulse-

height analyzer insured simulation of a monochromatic Mo$K\alpha$-beam. The intensities measured were symmetry related in pairs. All reflexions within a hemisphere of radius $\sin\theta/\lambda = 0.7$ were measured. The data were processed using an Algol program [5] which evaluated intensities, calculated averages, Lp corrections, and standard deviations. The latter were estimated as the square root of the total number of counts in an intensity measurement. Reflexions which were smaller than twice their standard deviation were considered not significantly different from zero. This left us with 1940 significant reflexions.

STRUCTURE DETERMINATION

The compound belongs to the monoclinic system. Reflexions $0k0$ were missing for $k = 2n+1$. A strong piezoelectric effect was detected using the Giebe-Scheibe method. Hence the space group $P2_1$ was indicated. The structure was determined from the three-dimensional Patterson function which was calculated using a program written by Lauesen.[6] The Harker section was obscured by non-Harker peaks. After one unsuccessful attempt of interpretation the germanium and four of the chlorine positions were located using image seeking methods.

The positional parameters found from the Patterson map were refined using the Bhuiya-Stanley method [7] employing a program D45 written by Danielsen.[8] An R-value of 34 % was obtained and a Fourier-synthesis based upon this trial structure was calculated. The Fourier map showed the atoms inserted in the structure factor calculations and two additional atoms which were assumed to be chlorine atoms. A new refinement gave an R-value of 29 % and the organic group was located in two successive Fourier maps. After 38 atoms were located in the asymmetric unit by Patterson and Fourier methods the R-value was 21.4 %. Further refinement was carried out at NEUCC in Lundtofte using the ORFLS program of Busing, Martin and Levy.[9] After three cycles of full-matrix least-squares refinement using isotropic temperature factors the R-value was 17.5 %.

Reflexions close to the spindle-axis cannot be measured precisely because of the low setting accuracy of the diffractometer and of the uncertainty of the Lorentz factor. Such reflexions were omitted from further computations. In the later least-squares calculations reflexions smaller than 2.5 times their standard deviations were left out and the computations were confined to reflexions within a hemisphere of radius $\sin\theta/\lambda = 0.60$. These restrictions left us with 1619 reflexions.

A difference Fourier map was computed at the end of the refinement employing isotropic temperature factors. It showed an atom with a peak height of 3 electrons, presumably a water molecule. It appeared in a hole in the structure and chemical analysis and the density of the crystal makes it likely that two water molecules per unit cell should be present.

Refinement was continued using anisotropic temperature factor parameters. The two molecules per asymmetric unit had to be refined alternately since the program can handle at most 180 parameters. Two atoms $C8_1$ and $C8_2$ acquired negative vibration amplitudes during refinement. We inserted $C8_1$ as nitrogen and $N2_1$ as carbon in the refinement. This caused the R-value to increase and the vibration amplitudes of the questionable atoms were still negative. Instead we adjusted the temperature factor parameters to physically

Table 1. Atomic coordinates as fractions of cell edges with their standard deviations.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Ge1	0.5289	(2)	0.0000	(0)	0.3874	(3)
Cl 1	0.3814	(4)	0.0389	(4)	0.2643	(9)
Cl 2	0.5602	(5)	−0.0594	(4)	0.1071	(10)
Cl 3	0.6038	(5)	0.1100	(4)	0.3247	(10)
C 1_1	0.2137	(19)	0.4240	(14)	0.5002	(37)
C 2_1	0.1932	(13)	0.3698	(12)	0.3243	(30)
C 3_1	0.2821	(14)	0.3500	(11)	0.2391	(24)
C 4_1	0.2665	(18)	0.2998	(16)	0.0544	(32)
C 5_1	0.4109	(14)	0.2679	(13)	0.2015	(27)
C 6_1	0.3626	(13)	0.3040	(11)	0.3692	(26)
C 7_1	0.3241	(14)	0.2440	(11)	0.4998	(23)
C 8_1	0.4044	(15)	0.2047	(13)	0.6256	(31)
C 9_1	0.4960	(15)	0.2187	(12)	0.6524	(30)
C10_1	0.4682	(17)	0.1198	(12)	0.8293	(24)
C11_1	0.2973	(17)	0.1073	(12)	0.7405	(34)
N 1_1	0.5383	(12)	0.1640	(14)	0.7879	(22)
N 2_1	0.3870	(11)	0.1394	(9)	0.7255	(20)
O 1_1	0.1959	(11)	0.3048	(9)	−0.0665	(22)
O 2_1	0.3363	(11)	0.2546	(8)	0.0334	(18)
O 3	0.7126	(15)	0.0813	(19)	0.9406	(40)
Ge2	0.1020	(2)	0.0215	(2)	0.2031	(4)
Cl 4	−0.0542	(6)	0.0157	(7)	0.0764	(11)
Cl 5	0.1105	(5)	0.1496	(4)	0.2180	(9)
Cl 6	0.0813	(5)	0.0030	(4)	0.5266	(10)
C 1_2	0.6437	(19)	0.3825	(13)	0.3044	(41)
C 2_2	0.6555	(13)	0.3282	(10)	0.1283	(31)
C 3_2	0.7487	(14)	0.3381	(9)	0.0613	(29)
C 4_2	0.7650	(16)	0.2897	(13)	−0.1089	(34)
C 5_2	0.9144	(14)	0.3120	(15)	0.0539	(32)
C 6_2	0.8420	(14)	0.3256	(11)	0.2078	(27)
C 7_2	0.8301	(14)	0.2538	(10)	0.3405	(25)
C 8_2	0.9144	(14)	0.2441	(12)	0.4805	(27)
C 9_2	0.9868	(15)	0.2906	(12)	0.5494	(29)
C10_2	1.0063	(18)	0.1805	(15)	0.7198	(34)
C11_2	0.8670	(18)	0.1073	(12)	0.5613	(37)
N 1_2	1.0418	(12)	0.2490	(10)	0.6919	(21)
N 2_2	0.9307	(13)	0.1739	(11)	0.5853	(27)
O 1_2	0.7079	(11)	0.2659	(12)	−0.2347	(23)
O 2_2	0.8551	(12)	0.2747	(10)	−0.1097	(22)

meaningful values and resumed refinement. The parameters mentioned did not go back to physically unacceptable values during the following refinement cycles and convergence was reached at an R-value of 7.8 %. The weights used were $w=1/(\mu F)^2$ where $\mu F=-F_o+\sqrt{\sigma F^2+(a+1)F_o^2}$. σF^2 is estimated from counting statistics and a was chosen so ($a=0.08$) that the weighted least-squares residual was independent of the size of F_o.

Correction for anomalous dispersion was not applied. The imaginary part of the structure factor for Ge is $\Delta f''=1.9$ for Mo$K\alpha$-radiation. Since we had averaged intensities of indices *hkl* and *hkl* the polar dispersion error in positional coordinates would be negligible. At the end of the structure analysis the computations were carried out using the program system X-ray-63 edited by Stewart.[10]

CRYSTAL DATA

Some relevant crystallographic data are given below:

Crystal system: monoclinic (b unique), $a=14.24$ Å, $b=17.61$ Å, $c=6.83$ Å, $\beta=97.3°$. Systematic absences: $0k0$ for $k=2n+1$. Space group $P2_1$ (No. 4) from absences of reflexions and from determination of piezoelectric effect. Formula: $C_{11}H_{17}N_2O_2,GeCl_3,\frac{1}{2}H_2O$. Four formula units per unit cell. Density calculated: 1.54 g/cm³, observed 1.54 g/cm³. Absorption coefficient for Mo$K\alpha$ radiation $\mu=23$ cm^{-1}.

Final atomic coordinates and temperature factor parameters are given in Tables 1 and 2. Interatomic distances and bond angles are given in Tables 3 and 4 and observed and calculated structure factors are given in Table 5.

Table 2. Temperature factor parameters as they appear in the expression $\exp-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)$.

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ge1	0.00674	0.00403	0.02995	0.00108	0.00059	0.00320
Cl 1	0.00550	0.00683	0.03717	0.00171	0.00352	0.00210
Cl 2	0.00751	0.00457	0.05112	0.00050	0.00223	−0.00877
Cl 3	0.00801	0.00372	0.04133	0.00025	−0.00136	−0.00260
C 1_1	0.00820	0.00373	0.04247	0.00280	0.00696	−0.00104
C 2_1	0.00152	0.00351	0.03473	0.00067	0.00539	0.00345
C 3_1	0.00387	0.00331	0.01506	0.00005	−0.00419	0.00088
C 4_1	0.00603	0.00562	0.02023	−0.00332	0.00335	−0.00273
C 5_1	0.00330	0.00477	0.02029	0.00041	−0.00095	0.00013
C 6_1	0.00285	0.00280	0.02270	0.00001	0.00427	−0.00063
C 7_1	0.00420	0.00330	0.01317	0.00024	0.00174	0.00310
C 8_1	0.00335	0.00467	0.02106	−0.00013	0.00357	−0.00062
C 9_1	0.00375	0.00398	0.02479	0.00085	0.00216	−0.00015
C10_1	0.00837	0.00491	0.01085	0.00304	0.00380	0.00290
C11_1	0.00680	0.00309	0.04307	−0.00150	0.00444	0.00204
N 1_1	0.00350	0.00618	0.01542	0.00028	0.00245	0.00181
N 2_1	0.00322	0.00278	0.01752	0.00052	0.00001	0.00188
O 1_1	0.00681	0.00543	0.02852	−0.00274	−0.00630	0.00169
O 2_1	0.00563	0.00316	0.02411	−0.00012	0.00408	−0.00069
O 3	0.00921	0.01513	0.09283	0.00377	0.01058	0.01613
Ge2	0.00888	0.00322	0.04997	0.00005	0.00401	−0.00333
Cl 4	0.00910	0.01127	0.04586	−0.00492	−0.00399	−0.00254
Cl 5	0.00844	0.00364	0.03719	−0.00165	−0.00282	0.00130
Cl 6	0.01180	0.00415	0.04629	−0.00030	−0.00239	0.00710
C 1_2	0.00772	0.00305	0.05838	0.00072	0.00979	−0.00514
C 2_2	0.00314	0.00166	0.03762	−0.00054	0.00316	0.00011
C 3_2	0.00464	0.00121	0.03165	0.00001	0.00017	−0.00353
C 4_2	0.00339	0.00463	0.03005	−0.00124	0.00014	0.00201
C 5_2	0.00254	0.00740	0.03005	−0.00312	0.00439	−0.00028
C 6_2	0.00431	0.00303	0.02002	−0.00105	−0.00351	0.00054
C 7_2	0.00507	0.00170	0.02015	−0.00092	−0.00345	0.00022
C 8_2	0.00395	0.00322	0.02402	−0.00067	0.00109	−0.00001
C 9_2	0.00369	0.00332	0.02510	−0.00006	0.00222	0.00100
C10_2	0.00685	0.00458	0.03053	0.00067	0.00281	−0.00142
C11_2	0.00782	0.00311	0.04343	−0.00062	−0.00312	0.00270
N 1_2	0.00587	0.00398	0.01718	0.00030	0.00317	−0.00276
N 2_2	0.00467	0.00416	0.02853	0.00072	−0.00289	−0.00104
O 1_2	0.00377	0.01064	0.03109	0.00063	−0.00171	−0.00351
O 2_2	0.00455	0.00691	0.03800	0.00056	0.00127	−0.00315

Table 3. Interatomic distances with their standard deviations. The distances are uncorrected for thermal vibration effects.

Atoms	Distances (Å)	Atoms	Distances (Å)
Ge1 —Cl1	2.268 (7)	$Cl0_1$—N 2_1	1.324 (25)
Ge1 —Cl2	2.275 (8)	N 2_1—$Cl1_1$	1.412 (28)
Ge1 —Cl3	2.277 (7)	N 2_1—C 8_1	1.376 (28)
Ge2 —Cl4	2.285 (8)	C 1_2—C 2_2	1.562 (33)
Ge2 —Cl5	2.261 (7)	C 2_2—C 3_2	1.468 (29)
Ge2 —Cl6	2.289 (8)	C 3_2—C 4_2	1.483 (31)
C 1_1—C 2_1	1.534 (32)	C 4_2—O 1_2	1.182 (27)
C 2_1—C 3_1	1.499 (28)	C 4_2—O 2_2	1.311 (29)
C 3_1—C 4_1	1.534 (29)	O 2_2—C 5_2	1.468 (26)
C 4_1—O 1_1	1.221 (27)	C 5_2—C 6_2	1.581 (30)
C 4_1—O 2_1	1.295 (31)	C 6_2—C 3_2	1.575 (26)
O 2_1—C 5_1	1.482 (22)	C 6_2—C 7_2	1.577 (26)
C 5_1—C 6_1	1.546 (28)	C 7_2—C 8_2	1.447 (26)
C 6_1—C 3_1	1.581 (25)	C 8_2—C 9_2	1.354 (28)
C 6_1—C 7_1	1.529 (26)	C 9_2—N 1_2	1.380 (25)
C 7_1—C 8_1	1.509 (27)	N 1_2—$Cl0_2$	1.330 (32)
C 8_1—C 9_1	1.316 (30)	$Cl0_2$—N 2_2	1.329 (29)
C 9_1—N 1_1	1.416 (27)	N 2_2—$Cl1_2$	1.480 (29)
N 1_1—$Cl0_1$	1.323 (29)	N 2_2—C 8_2	1.433 (27)

Table 4. Bond angles with their standard deviations.

Atoms	Angles (degrees)	Atoms	Angles (degrees)
Ge1 Cl1 Cl2	95.6 (0.3)	$Cl0_1$ N 1_1 N 2_1	111.3 (1.7)
Ge1 Cl1 Cl3	96.2 (0.3)	N 2_1 C 8_1 $Cl0_1$	106.5 (1.6)
Ge1 Cl2 Cl3	95.0 (0.3)	N 2_1 C 8_1 $Cl1_1$	126.3 (1.6)
		N 2_1 $Cl0_1$ $Cl1_1$	126.4 (1.7)
Ge2 Cl4 Cl5	96.1 (0.4)	C 2_2 C 1_2 C 3_2	110.9 (1.7)
Ge2 Cl4 Cl6	97.0 (0.3)	C 3_2 C 2_2 C 4_2	114.5 (1.7)
Ge2 Cl5 Cl6	96.4 (0.3)	C 3_2 C 2_2 C 6_2	120.6 (1.7)
		C 3_2 C 4_2 C 6_2	102.4 (1.6)
C 2_1 C 1_1 C 3_1	111.3 (1.7)	C 4_2 C 3_2 O 1_2	127.7 (2.2)
C 3_1 C 2_1 C 4_1	114.3 (1.7)	C 4_2 C 3_2 O 2_2	111.6 (1.8)
C 3_1 C 2_1 C 6_1	119.2 (1.5)	C 4_2 O 1_2 O 2_2	120.7 (2.2)
C 3_1 C 4_1 C 6_1	100.8 (1.6)	O 2_2 C 4_2 C 5_2	112.1 (1.8)
C 4_1 C 3_1 O 1_1	122.4 (2.3)	C 5_2 C 6_2 O 2_2	102.3 (1.5)
C 4_1 C 3_1 O 2_1	114.3 (1.8)	C 6_2 C 3_2 C 5_2	99.7 (1.5)
C 4_1 O 1_1 O 2_1	123.2 (2.1)	C 6_2 C 3_2 C 7_2	109.5 (1.5)
O 2_1 C 4_1 C 5_1	107.6 (1.6)	C 6_2 C 5_2 C 7_2	112.8 (1.7)
C 5_1 C 6_1 O 2_1	107.2 (1.5)	C 7_2 C 6_2 C 8_2	109.5 (1.6)
C 6_1 C 3_1 C 5_1	98.8 (1.4)	C 8_2 C 7_2 C 9_2	133.7 (1.9)
C 6_1 C 3_1 C 7_1	113.2 (1.5)	C 8_2 C 7_2 N 2_2	120.0 (1.7)
C 6_1 C 5_1 C 7_1	111.9 (1.6)	C 8_2 C 9_2 N 2_2	106.2 (1.6)
C 7_1 C 6_1 C 8_1	110.3 (1.6)	C 9_2 C 8_2 N 1_2	105.3 (1.8)
C 8_1 C 7_1 C 9_1	131.3 (2.1)	N 1_2 C 9_2 $Cl0_2$	113.0 (1.7)
C 8_1 C 7_1 N 2_1	119.6 (1.7)	$Cl0_2$ N 1_2 N 2_2	105.6 (2.0)
C 8_1 C 9_1 N 2_1	108.9 (1.8)	N 2_2 C 8_2 $Cl0_2$	109.7 (1.9)
C 9_1 C 8_1 N 1_1	107.2 (1.9)	N 2_2 C 8_2 $Cl1_2$	124.8 (1.7)
N 1_1 C 9_1 $Cl0_1$	105.7 (1.6)	N 2_2 $Cl0_2$ $Cl1_2$	125.3 (2.0)

Table 5. **Observed and calculated structure factors.**

H,0,0

1	115	122	500
3	172	182	500
4	736	731	500
5	714	714	500
6	489	497	500
7	227	271	500
8	131	105	0
10	217	231	0
11	223	255	0
12	137	101	500

H,1,0

1	283	292	329
2	908	1011	162
3	405	410	305
4	984	965	238
5	839	906	755
6	176	195	367
7	931	996	753
8	114	161	865
9	232	254	822
10	172	177	383
11	172	200	475
12	228	222	355
14	184	220	139

H,2,0

0	518	631	178
1	211	236	506
2	1326	1482	97
3	578	598	464
4	592	645	706
5	654	614	587
6	616	650	589
7	306	307	481
8	237	261	245
9	170	184	866
10	282	292	227
11	209	215	924
12	248	265	563
13	134	161	164

H,3,0

1	312	323	440
2	820	810	416
4	493	504	152
5	429	429	701
6	482	498	122
7	599	644	773
8	141	147	30
9	468	474	765
10	106	99	892
12	205	214	318
14	134	186	464

H,4,0

0	1552	1628	95
1	653	555	112
2	1188	1216	894
3	380	402	333
4	407	428	805
5	689	708	520
7	387	363	538
8	247	254	355
9	153	200	815
11	138	97	200

H,5,0

1	659	636	325
2	915	922	129
3	727	708	413
4	308	316	209
5	428	409	715
6	147	179	422
7	739	766	768
8	255	263	110
9	337	367	720
10	237	234	324
12	129	122	262

H,6,0

0	929	1009	944
1	642	608	109
2	820	802	37
3	490	517	459
4	189	171	785
5	596	679	564
6	247	250	551
7	476	516	614
8	227	207	988
9	115	112	920
10	106	107	261
11	244	293	49

H,7,0

1	580	547	384
2	462	414	290
3	602	591	418
4	379	402	166
5	333	349	864
7	777	803	876
8	129	157	704
9	285	306	783
10	146	188	178
11	253	252	573
12	234	272	314
14	148	108	395

H,8,0

0	1099	1146	106
1	586	605	249
2	456	479	80
3	192	198	551
4	431	473	693
5	536	588	563
6	262	272	796
7	262	255	623
9	208	204	308
10	132	139	119
11	132	137	278
12	125	133	630

H,9,0

1	328	351	511
2	374	394	350
3	462	474	530
4	438	444	399
5	171	153	62
6	189	195	926
7	302	277	985
8	157	154	991
9	205	218	759
11	220	223	629
13	187	154	650

H,10,0

0	639	647	189
1	117	103	388
2	330	348	65
3	230	234	594
4	462	467	845
5	190	209	675
6	266	275	776
7	182	186	612
8	105	113	174

H,11,0

1	148	144	639
2	333	372	436
3	138	122	777
4	231	251	315
6	137	144	62
7	144	134	802
8	129	154	46
9	272	272	773
11	168	228	714

H,12,0

0	532	545	154
1	120	131	132
2	246	227	77
3	152	160	497
4	202	211	906
5	340	364	528
6	239	271	812
7	105	162	362
8	125	179	598
9	111	109	123
10	161	116	477

H,13,0

1	97	94	135
2	295	317	378
4	301	307	452
5	143	171	822
6	157	139	213
7	217	239	794
8	138	172	111

H,14,0

0	261	287	235
1	243	264	324
2	247	242	111
3	236	268	561
4	282	307	931
5	211	235	669
6	143	172	729

H,15,0

1	226	207	614
2	244	256	476
3	217	240	482
4	109	148	366
6	167	147	155
7	267	257	921
8	187	146	174

H,16,0

0	167	195	98
1	210	215	410
2	158	128	36
3	133	87	665
4	188	195	939
8	138	120	508

H,17,0

1	152	176	585
3	262	251	715

H,18,0

1	213	231	431

H,19,0

2	163	115	475
3	149	115	762

H,20,0

2	137	44	57

H,0,1

-13	254	199	500
-12	235	262	0
-11	165	156	0
-8	282	264	500
-7	479	452	500
-6	645	585	500
-5	564	550	500
-4	591	634	0
-3	122	76	0
-2	175	117	0
-1	564	684	0
0	94	110	500
1	128	180	500
2	1463	1567	500
3	226	227	0
4	583	633	500
5	413	398	0
7	935	961	0
9	316	316	0
10	294	285	500
11	236	184	500
12	184	204	500
13	191	61	500

H,1,1

-14	159	102	794
-11	166	150	648
-10	264	252	280
-8	570	575	289
-7	231	220	904
-6	191	220	854
-5	128	111	731
-4	756	756	983
-3	456	424	856
-2	963	976	163
-1	220	166	583
0	920	1098	263
1	102	58	412
2	839	783	195
3	501	530	678
4	1284	1259	859
5	401	423	713
6	653	712	786
7	130	153	823
9	374	384	218
11	301	280	319
13	154	177	179
14	165	180	805

H,2,1

-12	204	157	25
-10	160	185	138
-9	214	254	413
-8	341	356	695
-7	351	374	546
-6	276	250	941
-5	464	429	593
-4	312	302	177
-3	909	885	86
-2	1053	1033	92
-1	550	580	65
0	539	559	657
1	341	373	37
2	693	673	689
3	485	468	884
4	393	427	481
5	683	705	994
6	659	662	382
7	585	607	989
8	343	358	326
12	192	199	671

H,3,1

-10	142	120	382

Table 5. Continued.

H, 3, 1

-9	295	294	877
-8	309	312	372
-7	417	447	774
-6	385	364	285
-5	267	265	702
-4	492	531	242
-3	428	397	122
-2	1170	1121	284
-1	411	378	579
0	1883	1806	309
1	846	817	699
2	227	220	150
3	824	775	612
4	776	776	869
5	236	252	756
6	511	474	877
7	197	207	22
8	256	264	537
9	132	107	243
10	270	296	545
11	438	458	234
13	176	178	236

H, 4, 1

-12	161	142	249
-9	187	204	568
-8	128	133	130
-7	692	726	621
-5	252	235	697
-4	205	211	465
-3	545	555	53
-2	1300	1289	614
-1	1066	1031	119
0	697	635	324
1	175	158	366
2	154	86	936
3	271	264	819
4	606	601	469
5	799	859	961
6	298	293	568
7	702	676	997
9	182	199	878
11	163	234	614

H, 5, 1

-14	159	181	878
-12	184	200	910
-11	173	183	384
-10	190	200	302
-8	381	404	352
-7	306	304	848
-6	443	479	256
-5	612	613	726
-4	211	243	174
-3	346	322	785
-2	594	517	407
-1	341	333	198
0	630	553	227
1	91	120	261
2	261	197	700
3	390	395	680
4	428	421	988
5	545	514	693
6	415	442	841
7	202	198	976
8	219	266	765
9	335	361	229
12	180	255	636
13	167	181	456

H, 6, 1

-15	185	152	617
-12	223	252	999
-10	177	175	927
-9	249	265	622
-7	427	415	592
-5	130	173	963
-4	206	254	797
-3	753	774	136
-2	117	113	725
-1	975	905	117
0	308	292	696
1	248	298	969
2	813	833	443
3	248	247	606
4	378	380	497
5	260	289	982
6	138	60	708
7	332	354	49
8	184	196	133
9	136	152	82
10	171	192	279
11	202	196	669

H, 7, 1

-12	191	160	976
-8	215	285	316
-7	343	362	827
-6	313	311	254
-5	896	878	875
-4	294	287	149
-3	341	353	677
-2	865	865	207
-1	464	458	493
0	523	513	389
1	365	391	381
3	225	224	813
4	597	630	848
5	397	415	898
6	433	469	841
9	221	219	236
-13	163	166	698
-12	159	160	976
-11	179	142	728
-10	175	168	228
-8	275	285	316
-7	347	362	827
-6	321	311	254
-5	911	878	875
5	413	415	898
6	419	469	841
8	142	145	480
9	208	219	236
11	190	187	375
14	161	122	752

H, 8, 1

-13	151	124	370
-12	144	158	45
-11	223	242	472
-10	230	245	60
-9	248	253	529
-8	105	120	879
-7	375	404	705
-6	265	281	685
-5	252	244	757
-4	132	123	727
-3	523	492	176
-2	298	306	126
-1	691	684	186
0	667	664	449
1	517	506	834
2	637	664	527
3	843	841	853
4	309	298	654
5	379	372	977
6	254	258	67
7	335	313	142
8	211	197	159
9	155	182	961
10	197	228	462
11	232	233	726
12	167	200	515

H, 9, 1

-10	129	150	485
-9	245	222	588
-8	233	250	412
-7	197	202	655
-6	365	361	205
-5	214	223	805
-4	688	722	170
-3	351	386	886
-2	353	358	264
-1	189	203	473
0	669	648	425
1	398	421	514
2	124	96	751
4	455	469	868
5	285	269	983
6	367	376	901
7	167	152	157
9	190	172	400
10	174	193	606
11	177	156	373
13	114	64	242

H, 10, 1

-11	267	281	407
-10	142	123	32
-9	121	122	423
-8	161	206	767
-7	238	257	731
-6	182	168	872
-5	247	246	786
-4	285	228	191
-2	419	425	317
-1	200	172	105
0	451	463	463
1	570	559	77
2	567	577	558
3	336	344	958
4	225	209	717
6	132	136	476
7	145	115	245
8	128	173	362
11	150	132	997

H, 11, 1

-12	123	98	22
-7	187	224	755
-6	220	236	126
-5	105	117	728
-4	435	457	170
-3	331	323	670
-2	464	490	314
-1	296	272	791
0	274	259	494
1	202	217	668
2	262	246	611
4	271	265	17
6	221	236	954
8	163	156	735
9	112	97	457
11	144	139	471

H, 12, 1

-13	121	87	475
-9	155	155	495
-8	170	168	903
-7	122	104	668
-6	121	103	917
-5	198	246	878
-4	124	117	265
-3	211	247	31
-2	340	385	369
-1	115	94	408
0	255	262	467
1	170	167	841
2	213	204	618
3	261	259	994
4	223	220	604
5	217	222	996
6	110	83	64
7	214	226	36
9	144	111	39

H, 13, 1

-9	113	119	469
-6	195	242	155
-5	279	310	753
-4	347	359	157
-3	147	150	946
-2	182	161	204
0	305	285	454
2	127	126	448
3	213	238	775
4	207	218	948
5	169	154	906
6	109	97	21
7	162	140	121
8	126	87	752
9	217	218	272
10	151	111	778

H, 14, 1

-10	113	58	39
-8	214	211	845
-6	126	145	754
-2	243	256	284
-1	211	221	128
0	189	160	475
1	113	125	745
2	264	258	593
3	287	280	868
4	148	175	593
5	245	220	39
7	165	185	130
8	161	156	399

H, 15, 1

-6	144	169	163
-5	197	199	972
-4	279	295	197
-2	177	189	273
-1	291	313	520
1	253	269	629
3	186	194	811
5	260	262	986
6	155	168	48
7	172	181	299
8	127	123	816
9	152	184	399
10	127	130	689
11	145	104	457

H, 16, 1

-7	146	140	858
-6	209	191	915
-3	196	187	384
-2	151	193	355
-1	179	182	464
0	203	252	391
1	117	112	982
2	112	97	768
3	269	282	952
4	134	112	723
5	194	169	985
6	126	128	344

H, 17, 1

-6	129	48	459
-4	161	181	220
-2	121	130	201
-1	194	221	696
0	121	77	677

Table 5. Continued.

H,17,1

1	246	276	678
3	133	114	971
5	155	143	146
9	123	84	543

H,18,1

-7	121	73	995
-6	122	122	909
-2	117	69	560
-1	120	130	482
1	132	118	925
2	122	127	578
3	146	165	961
5	136	101	32

H,19,1

-2	150	127	296

H,0,2

-14	159	63	0
-13	193	216	0
-11	206	197	0
-10	443	447	500
-9	302	280	0
-8	554	524	500
-7	406	371	500
-6	512	414	500
-4	589	543	0
-3	386	386	0
-2	311	236	500
-1	694	782	0
0	567	586	500
3	311	329	500
4	831	753	0
5	141	126	500
6	553	574	0
8	259	220	500
10	134	165	500
11	332	327	500
12	332	321	0
13	216	202	500

H,1,2

-15	163	162	704
-14	154	142	293
-12	175	188	422
-11	237	192	279
-9	244	216	225
-8	356	321	693
-7	468	439	914
-6	540	483	774
-5	118	120	806
-4	580	480	657
-3	1112	1018	391
-2	828	755	490
-1	1509	1634	285
0	136	157	306
1	466	483	336
2	295	284	838
3	319	317	831
4	654	573	799
5	552	478	36
6	290	271	815
7	279	279	427
8	112	98	625
11	224	209	853
13	124	126	857

H,2,2

-12	189	156	318
-11	133	118	49
-10	420	405	559
-9	239	221	691
-8	803	784	550
-7	253	236	972
-6	360	334	382
-5	158	191	908
-4	552	552	996
-3	348	344	266
-2	618	589	848
-1	486	503	259
0	726	718	735
1	282	289	763
2	224	226	982
3	434	372	619
4	597	596	119
5	115	97	659
6	368	351	78
7	152	147	173
8	333	333	892
9	277	264	513
10	227	204	836
11	267	281	556
13	162	135	608
14	156	124	164

H,3,2

-15	142	147	905
-12	157	153	254
-11	186	169	380
-10	108	114	940
-9	141	123	266
-8	243	239	700
-6	482	457	830
-5	537	527	41
-4	365	389	704
-3	868	770	168
-2	644	559	904
-1	1428	1318	422
0	329	308	944
1	508	491	304
2	351	280	82
3	313	284	162
4	437	410	924
5	198	188	781
6	481	457	630
7	177	172	154
8	146	119	575
11	145	114	857
13	129	99	625

H,4,2

-13	180	194	942
-12	131	91	291
-10	226	216	491
-9	135	165	988
-8	505	499	485
-7	209	186	977
-6	411	379	567
-5	275	250	110
-4	375	377	361
-3	401	379	28
-2	484	478	54
-1	287	299	146
0	520	542	996
1	516	506	457
2	171	123	385
3	141	151	691
4	396	392	151
5	357	337	640
6	563	573	89
7	365	357	477
8	222	213	980
9	221	224	369
10	165	161	890

H,5,2

-15	145	126	720
-9	127	123	745
-8	108	57	451
-7	407	404	933
-6	360	379	662
-5	183	159	199
-4	464	458	774
-3	747	702	383
-2	304	276	543
-1	707	662	233
0	151	153	162
1	511	446	338
2	266	271	681
3	356	346	54
4	391	370	688
5	252	242	161
6	357	367	830
7	131	148	949
9	162	159	866
10	271	268	396
11	191	188	782

H,6,2

-12	166	124	261
-11	170	174	852
-10	212	197	514
-9	193	184	615
-8	605	576	586
-7	214	144	208
-6	623	625	544
-5	563	538	13
-4	105	73	322
-3	516	435	91
-2	114	97	109
-1	354	315	578
0	336	342	641
1	236	187	798
2	237	191	22
3	260	257	635
4	622	597	7
5	154	136	614
6	463	432	55
7	152	132	539
8	230	208	57
9	377	358	530
11	271	264	566
12	132	115	769

H,7,2

-11	129	144	431
-10	242	226	308
-9	111	104	69
-8	165	162	860
-7	407	386	949
-6	276	300	784
-5	395	372	952
-4	338	323	708
-3	916	882	304
-2	103	106	813
-1	993	911	359
0	583	561	605
1	819	792	250
2	507	451	710
3	362	339	49
4	588	584	839
5	117	125	211
6	286	244	932
7	172	153	391
8	175	160	464
9	122	132	805
10	139	127	487

H,8,2

-14	148	124	206
-12	146	144	191
-10	284	246	512
-9	188	158	898
-8	453	442	642
-5	141	137	178
-4	468	444	305
-3	657	619	42
-2	218	193	278
-1	420	374	58
0	431	406	678
1	520	479	607
2	484	464	865
3	404	398	502
4	450	428	152
5	298	286	362
6	546	509	155
7	232	202	445
8	185	158	940
9	186	186	699
10	141	177	780

H,9,2

-11	146	164	562
-7	367	397	22
-6	218	247	866
-5	182	168	72
-4	190	144	920
-3	334	306	521
-2	608	599	631
-1	637	620	376
0	354	325	611
1	531	489	203
2	467	466	839
3	517	482	143
4	288	266	842
5	203	192	977
6	248	254	175
7	246	224	651
8	145	158	361
9	167	154	684
11	163	176	897

H,10,2

-12	179	177	466
-8	190	160	705
-7	185	190	773
-6	272	282	444
-5	308	331	68
-4	474	474	352
-3	150	163	159
-2	263	227	422
-1	261	233	927
0	324	314	898
1	103	104	954
2	431	437	919
3	280	274	588
4	320	298	103
5	318	282	461
7	174	152	294
8	181	200	919
9	205	200	424
10	169	162	954

H,11,2

-8	204	205	7
-7	206	212	395
-6	224	219	929
-5	288	273	76
-4	155	166	707
-3	166	127	165
-2	268	295	558
-1	375	341	373
0	347	346	707
1	361	342	268
2	238	222	708
3	551	525	185
5	167	164	108
7	177	160	818
8	153	121	657

H,12,2

-10	173	153	695

Table 5. Continued.

H, 12, 2

-7	141	149	841
-6	231	216	385
-5	160	118	954
-4	266	297	434
-3	214	182	53
-2	130	96	348
-1	135	100	421
0	217	207	925
1	223	221	681
3	155	132	737
5	200	216	382
7	361	360	474
8	163	162	38
9	131	112	426
10	167	155	911
11	141	143	633

H, 13, 2

-8	158	148	962
-7	228	216	47
-6	220	177	949
-4	146	144	679
-3	186	168	384
-2	231	238	529
-1	142	145	414
0	293	304	590
1	228	203	297
2	188	164	887
3	162	179	96
4	169	157	907
5	256	279	87

H, 14, 2

-8	196	156	661
-5	168	200	131
-4	242	242	264
-3	127	77	162
-2	173	131	194
-1	123	163	800
1	202	190	747
2	130	126	864
6	151	157	113
7	149	158	356
9	199	192	625

H, 15, 2

-6	133	181	957
-5	246	225	205
-4	247	219	795
-2	280	271	669
-1	182	178	579
0	195	222	524
1	178	205	33
3	307	316	141
5	189	148	255

H, 16, 2

-9	194	166	918
-5	179	130	422
-4	169	191	348
-3	163	155	314
-2	143	137	282
-1	164	150	772
0	224	165	935
1	237	222	811
2	164	137	881
5	214	206	425
7	159	147	463

H, 17, 2

-7	171	174	233
-5	158	117	265
-3	185	164	571
-2	136	179	642
0	151	162	730
1	151	125	302
3	206	210	179

H, 18, 2

0	143	85	87
2	150	139	0

H, 19, 2

-1	143	50	624
3	131	72	249

H, 0, 3

-13	149	103	500
-11	246	236	500
-10	179	163	0
-9	294	318	500
-8	478	471	0
-6	598	638	0
-4	406	422	0
-3	547	512	500
-2	54	53	500
3	720	804	0
4	159	137	0
5	838	872	0
8	245	246	500
9	351	331	500
10	172	189	500

H, 1, 3

-13	142	154	284
-11	133	140	373
-10	333	322	772
-9	120	118	989
-8	483	484	772
-7	239	229	21
-6	125	84	134
-5	207	219	164
-4	742	770	274
-3	465	455	422
-2	629	717	237
-1	199	306	881
0	200	230	100
1	718	798	778
2	74	67	210
3	698	699	696
4	555	546	326
5	123	101	960
6	461	427	305
7	128	129	355
11	114	115	684

H, 2, 3

-15	133	118	29
-11	178	207	652
-10	103	41	124
-9	379	421	603
-8	272	254	75
-7	227	223	227
-6	265	265	961
-5	459	460	298
-4	244	238	997
-3	710	705	491
-2	164	173	699
-1	697	780	526
0	150	184	477
1	355	340	673
2	216	208	165
3	725	711	88
4	208	211	969
5	368	383	79
6	130	129	919
7	236	226	5
8	210	174	584
9	197	218	967

H, 2, 3

10	183	174	453
13	121	124	137

H, 3, 3

-15	120	106	386
-11	112	104	65
-10	288	287	731
-8	386	360	783
-7	162	156	873
-6	263	255	706
-5	295	287	479
-4	474	488	338
-3	220	226	347
-2	525	528	248
-1	462	457	600
0	347	362	68
1	337	326	850
2	194	176	257
3	651	612	861
4	187	162	304
5	516	525	743
6	191	194	315
7	99	109	684
8	121	113	278
11	166	141	899

H, 4, 3

-11	218	210	497
-9	110	82	300
-8	132	136	961
-7	121	80	271
-6	578	582	899
-5	329	323	411
-4	511	476	933
-3	809	781	510
-2	368	336	916
-1	661	643	562
0	133	131	479
1	121	96	631
2	118	89	978
3	241	263	70
4	384	387	89
5	230	214	67
6	325	321	74
7	183	150	875
8	165	148	619
9	150	113	761
10	430	388	567
11	139	132	98
12	198	212	567

H, 5, 3

-11	131	114	846
-10	164	138	738
-9	161	184	112
-8	352	362	850
-7	169	147	243
-6	139	133	318
-5	318	302	106
-4	608	574	232
-3	157	146	725
-2	545	543	240
-1	411	363	476
0	204	216	90
1	490	460	659
2	212	213	986
3	465	458	748
4	332	304	360
5	172	182	55
6	445	437	278
7	113	86	920
8	237	229	169
9	130	94	714
11	111	94	627
13	118	67	103

H, 6, 3

-11	215	203	654
-9	157	143	590
-8	276	274	960
-7	272	266	288
-6	370	348	23
-5	240	229	274
-4	212	220	46
-3	495	462	587
-2	170	173	457
-1	755	734	566
0	113	134	532
1	205	190	257
2	232	216	996
3	208	210	51
4	451	454	98
5	273	261	19
6	234	245	357
7	195	185	900
8	289	271	470
9	189	210	80
10	175	200	653
11	115	113	983

H, 7, 3

-15	130	96	333
-13	148	112	238
-12	187	163	611
-10	134	101	842
-9	328	350	798
-8	243	225	809
-7	114	99	923
-5	255	224	365
-4	545	504	435
-3	412	420	267
-2	548	490	407
-1	332	305	806
0	276	283	25
1	644	643	752
2	395	397	991
3	352	343	771
4	382	390	201
5	192	181	765
6	367	344	319
7	120	112	536
8	210	201	393
9	169	193	684
10	179	159	9

H, 8, 3

-11	142	147	606
-10	123	111	745
-9	155	132	507
-8	108	98	31
-6	427	450	95
-5	164	157	230
-3	205	204	563
-2	403	401	672
-1	399	385	562
0	384	388	798
1	298	283	451
2	254	262	29
3	423	430	244
4	307	290	95
5	396	384	35
6	107	57	297
7	126	146	924
8	254	244	661
9	148	119	828
10	229	225	611

H, 9, 3

-13	120	114	388
-11	118	91	115
-10	162	114	839
-8	179	170	0

Table 5. Continued.

H, 9, 3

-7	203	182	899
-5	164	173	288
-4	333	296	478
-3	220	224	364
-2	187	154	485
0	212	214	150
1	374	362	859
2	281	276	118
3	245	225	802
4	227	240	319
5	336	332	621
6	220	214	395
7	177	177	669
8	182	186	142
10	115	104	45
11	157	129	832

H, 10, 3

-12	123	88	933
-10	120	109	996
-8	254	252	133
-7	174	181	381
-5	163	182	384
-3	194	182	577
-2	194	182	759
-1	330	322	661
0	284	258	847
1	339	356	484
2	166	190	124
3	322	293	232
4	176	157	261
5	225	221	230
7	163	195	992
12	179	114	474
7	153	195	992

H, 11, 3

-8	194	180	44
-6	168	189	267
-4	261	271	442
-3	176	176	487
-1	129	128	824
0	148	149	71
1	255	252	824
2	194	202	231
3	311	297	860
4	139	153	196
5	102	84	769
6	138	155	209
7	159	165	527
8	111	111	116

H, 12, 3

-8	151	159	1
-6	238	235	59
-5	172	183	494
-4	132	149	990
-3	168	128	534
-1	154	125	642
0	125	140	677
1	127	117	150
2	160	159	832
3	197	219	283
4	140	143	11
5	209	205	185
7	116	89	.5
9	166	135	947
10	123	119	583

H, 13, 3

-12	131	78	720
-4	177	197	384
-3	124	83	555
-2	189	196	334
-1	258	267	811
0	143	117	336
1	261	265	899
2	114	75	122
3	115	64	763
4	108	110	548
5	115	135	468
7	146	163	569
8	129	133	174

H, 14, 3

-8	118	103	110
-6	266	267	129
-5	201	207	463
-4	115	96	136
-3	238	240	634
-2	201	211	736
-1	176	170	620
0	114	134	679
3	229	234	240
5	135	110	280
8	140	130	704

H, 15, 3

-9	130	111	99
-5	160	158	472
-4	142	145	438
-2	204	184	403
-1	122	176	882
0	155	165	150
1	228	236	947
2	156	121	32

H, 16, 3

-7	128	136	441
-4	118	45	72
-3	146	114	662
-1	124	122	839
4	135	172	382

H, 17, 3

-3	138	115	696
2	181	177	228

H, 18, 3

-7	133	66	379
0	123	57	889

H, 0, 4

-10	126	121	0
-9	139	114	0
-7	245	231	0
-6	227	210	500
-5	187	188	500
-4	458	471	500
1	595	676	0
2	76	73	500
3	769	763	0
4	163	174	500
7	107	85	500
8	115	121	0
10	221	229	0

H, 1, 4

-15	121	114	406
-11	263	271	671
-10	147	134	50
-9	246	232	763
-6	139	137	219
-5	167	176	406
-4	105	117	166
-3	381	411	704
-2	113	160	176
0	43	56	595

H, 1, 4

1	159	173	290
3	594	587	279
4	143	138	579
5	389	376	200
6	136	143	731
7	96	80	26
8	274	270	752
9	109	83	802
10	194	201	758

H, 2, 4

-9	119	113	314
-8	245	258	25
-7	110	107	175
-6	94	61	462
-5	355	338	44
-4	537	511	541
-3	170	171	779
-2	322	378	522
-1	222	331	905
0	203	243	365
1	318	342	41
2	196	197	340
3	223	231	167
4	185	192	587
5	113	103	905
6	169	151	510
7	218	224	600
8	125	130	110
9	129	98	341

H, 3, 4

-13	115	101	728
-11	244	244	956
-10	156	149	374
-9	205	203	807
-8	211	205	216
-7	172	174	639
-6	237	233	164
-5	242	243	579
-4	220	224	179
-3	89	69	15
-2	138	148	431
-1	108	115	970
0	86	87	607
1	275	296	243
2	162	151	702
3	459	456	262
4	110	81	646
5	335	330	329
6	217	225	744
7	245	242	80
8	131	144	691
9	174	154	101
10	169	159	811

H, 4, 4

-9	161	173	2
-8	112	108	520
-7	214	229	349
-6	224	203	612
-4	349	347	541
-3	343	332	995
-2	425	416	526
-1	335	329	933
0	168	161	443
1	248	239	908
2	199	197	209
3	266	283	992
4	183	199	446
5	128	117	974
6	87	69	404
9	183	167	739
12	154	114	28

H, 5, 4

-12	131	96	600
-11	180	176	790
-9	239	210	848
-7	176	143	772
-6	174	159	271
-5	209	199	507
-3	225	236	620
-2	269	271	819
0	236	215	878
1	198	191	331
2	167	179	985
3	253	238	285
4	138	155	66
5	263	269	197
6	229	225	572
7	117	100	382
8	345	328	752
10	205	206	740

H, 6, 4

-10	113	90	826
-8	246	243	113
-7	270	251	995
-6	174	170	389
-5	99	99	109
-4	518	450	603
-3	88	133	404
-2	262	230	594
-1	198	203	981
0	135	116	319
1	385	385	949
2	177	170	190
3	113	98	811
4	157	171	309
5	154	125	113
6	209	200	566
10	114	100	902

H, 7, 4

-12	151	135	213
-11	132	143	858
-9	203	194	875
-8	136	111	266
-6	182	193	157
-5	92	75	773
-4	214	199	309
-3	138	119	569
-2	186	174	805
-1	130	133	660
0	218	231	933
1	202	195	316
2	220	216	314
3	449	427	317
4	239	235	448
5	134	85	280
7	179	188	992
8	218	234	794
10	160	143	875

H, 8, 4

-10	127	96	300
-9	130	77	134
-8	304	308	390
-7	189	188	5
-6	260	238	490
-4	383	395	602
-3	255	230	912
-2	225	190	617
-1	168	173	834
0	175	175	190
1	243	232	954
2	355	373	321
3	318	308	81
4	186	168	519
5	170	159	500
7	128	139	582

Table 5. Continued.

H, 8, 4

8	140	133	48
9	136	106	923
10	156	122	137

H, 9, 4

-11	160	153	809
-10	134	103	196
-9	130	133	883
-8	206	214	190
-7	104	102	739
-6	171	166	503
-5	255	266	530
-4	147	131	666
-2	96	92	921
-1	234	224	23
0	127	152	952
1	171	147	333
2	207	209	969
3	221	193	408
4	130	100	545
5	189	183	269
6	238	237	673
7	153	154	141
8	123	79	870

H, 10, 4

-6	177	183	517
-4	188	165	675
-3	131	94	830
-2	155	196	719
-1	286	289	1
0	260	248	484
1	287	277	117
2	144	115	454
7	175	159	784

H, 11, 4

-10	131	92	231
-6	139	168	325
-5	145	121	707
-3	138	119	665
-2	138	121	729
-1	110	116	331
1	201	196	241
3	171	182	395
4	166	126	871
5	209	166	394

H, 12, 4

-6	156	136	406
-5	119	106	658
-3	165	164	976
-2	178	161	595
-1	207	206	963
1	184	163	60
3	147	104	339
4	142	121	332
7	153	107	754
8	154	110	231

H, 13, 4

-2	117	93	737
-1	173	167	117
3	226	196	322
5	152	102	305
8	136	118	810

H, 14, 4

-6	129	108	431
-3	186	187	876
-1	237	239	35
1	190	149	101
2	134	134	393

H, 15, 4

1	166	133	337
3	157	150	361

H, 16, 4

-3	152	133	937
-1	148	170	989

H, 17, 4

4	168	110	739

H, 0, 5

-11	196	167	0
-9	168	193	0
-6	118	115	500
-5	291	316	500
-3	145	190	500
2	358	373	0
3	311	338	500
4	118	92	0
5	261	265	500
6	210	188	0

H, 1, 5

-12	124	139	677
-10	147	121	791
-9	183	160	240
-7	168	163	397
-5	135	164	188
-4	170	175	735
-3	98	114	14
-2	129	243	739
1	108	122	272
2	156	161	283
3	116	99	310
5	187	182	999
6	144	128	110
7	242	222	878
11	131	50	783

H, 2, 5

-11	158	115	119
-9	183	185	126
-7	164	150	588
-6	102	94	996
-5	254	269	589
-4	80	76	655
-3	111	136	571
-2	55	83	167
-1	50	118	263
0	165	200	108
2	169	155	3
3	306	304	635
4	263	284	65
5	129	127	600
8	145	130	10

H, 3, 5

-10	142	103	805
-7	167	174	258
-6	179	191	692
-5	93	94	322
-4	212	255	829
-2	130	158	812
2	79	85	564
3	98	117	224
4	211	217	402
9	119	134	766
11	143	115	633

H, 4, 5

-5	103	89	622
-3	162	178	574
-1	199	221	499
0	93	97	33
1	332	302	492
2	271	243	117
4	97	92	952

H, 5, 5

-9	111	99	271
-7	185	194	205
-5	258	272	327
-4	280	286	791
-3	157	168	278
-2	184	203	801
-1	127	127	18
1	126	140	920
2	183	245	424
7	150	116	921
8	125	106	250
9	163	113	822

H, 6, 5

-5	101	169	604
-3	208	214	540
-2	191	190	937
-1	121	141	497
0	317	335	49
2	206	169	94
3	167	171	501
5	177	199	421
6	181	197	868

H, 7, 5

-9	151	131	179
-6	161	138	645
-7	155	179	336
-5	117	150	304
-4	280	297	886
-2	283	265	873
0	110	125	631
1	116	116	210
2	119	131	349
4	154	149	450
5	123	149	746

H, 8, 5

-10	134	44	296
-9	151	193	98
-6	117	113	671
-5	134	185	623
-3	120	156	562
0	148	169	149
1	272	223	469
2	138	111	116
4	195	199	934
8	129	71	993
9	130	83	130

H, 9, 5

-9	130	98	356
-6	157	179	594
-5	115	59	223
2	181	202	531
3	141	133	558
4	167	174	312
7	148	112	934

H, 10, 5

-11	134	52	118
-1	254	225	427
0	131	118	64
1	171	185	379
2	153	171	63
6	129	90	40

H, 11, 5

-5	143	150	192
-3	192	221	97
-1	121	159	89
8	136	110	239

H, 12, 5

-7	126	96	875
-5	134	113	753
-2	118	88	920
1	184	183	512
3	145	110	493

H, 13, 5

-4	137	100	727
-1	131	131	202

H, 14, 5

6	170	122	987

H, 15, 5

-3	133	145	90

H, 0, 6

-12	195	153	0
-7	164	149	500
-4	122	128	0
0	77	91	500
4	228	216	500

H, 1, 6

-7	216	170	799
-6	107	135	266
-5	258	259	766
-4	77	72	980
0	142	189	371
1	88	98	452
2	173	172	239
7	129	105	436

H, 2, 6

-4	93	53	132
0	73	96	484
1	117	142	887
2	287	281	564
6	124	101	486
7	180	115	82

H, 3, 6

-7	111	36	765
-5	199	212	827
-4	98	89	327
-3	180	195	771
-2	116	150	113
-1	97	122	662
0	189	230	232
2	169	174	369
3	100	76	984
4	124	100	135

H, 4, 6

-6	119	43	987
-5	105	110	551
-4	112	99	31
1	102	113	55
2	174	188	417
4	209	197	598

Table 5. Continued.

H,4,6				H,13,6				H,4,7				
7	129	76	89	-2	154	100	293	-6	77	80	494
								-5	79	87	995
H,5,6				H,0,7				-2	111	127	387
								4	97	66	950
-7	135	67	780	-7	94	69	0				
-5	128	148	736	-5	126	125	0	H,5,7			
-4	100	109	134	2	97	58	0				
-3	137	143	725					-9	99	63	575
-2	144	136	316	H,1,7				0	103	87	708
2	128	123	277					1	77	54	228
				-9	95	44	818	4	96	72	596
H,6,6				-6	72	69	825				
				-3	47	86	216	H,6,7			
-4	106	69	147	0	68	110	669				
0	161	188	512	1	91	90	191	-5	95	91	20
2	230	214	648	2	143	157	774	-3	98	83	25
				3	74	76	256				
H,7,6				4	92	102	878	H,7,7			
-5	154	148	850	H,2,7				-6	88	40	899
-3	131	102	790					-4	85	56	505
-2	168	139	194	-7	90	78	924	2	131	131	736
0	278	259	274	-5	79	87	37	4	93	67	640
2	170	125	295	2	84	121	572				
				3	74	65	325	H,8,7			
H,8,6				6	102	82	48				
								4	98	48	132
-1	176	133	147	H,3,7							
0	152	120	865					H,9,7			
2	156	120	621	-2	145	156	621				
6	147	117	391	-1	76	91	256	-6	97	61	884
				0	67	99	794	-4	95	54	838
H,9,6				5	88	26	473	-3	92	70	260
								-2	95	58	778
-4	145	94	85					0	94	57	745

DISCUSSION

The occurrence of two probably identical groups in the asymmetric unit prompts us to test our hypothesis of the equivalence of the molecules using the standard deviations obtained from the least-squares analysis. We have tested the hypothesis that all six Ge—Cl distances are equal using a multiple comparison test. In the following we use the notation of Hamilton.[11] The contrasts θ_n are defined as $\theta_n=|(x_i-x_j)|$ where x is a Ge—Cl distance. The confidence interval for the contrasts is

$$\theta_n - S\sigma_{\theta n} < \theta_n < \theta_n + S\sigma_{\theta n}$$

where $S^2=\chi^2_{n-1,0.05}$. For $n=6$ $S^2=11$. χ^2 is the usual chi-square distribution. Zero is included in all the confidence intervals. This supports our hypothesis about the equality of the distances. A two sample test at the 5 % level would have rejected, perhaps incorrectly, the hypothesis that Ge2—Cl5 and Ge2—Cl6 are equal.

It is more difficult to test the equivalence of the two pilocarpine molecules. A test for congruence between two polyhedra is mathematically complicated. We simply have made two sample "Student" t-tests on equivalent distances in the two molecules. We consider two corresponding bond lengths x_1 and x_2 to differ significantly only if $|x_1-x_2|>1.96\sigma(x_1-x_2)$. None of the differences exceeded this limit. A multiple comparison test may be based upon the following considerations.

The differences between two corresponding bond lengths $x_1-x_2=\Delta_i$ are supposed to belong to a set of mean values with the common value zero. We can form a multitude of contrasts based upon the Δ_i's and we find that a 95 % confidence interval for linear contrasts with coefficients numerically equal to one will include zero. This does not prove that our hypothesis about the equality of the two molecules is correct. Alternative hypotheses are also consistent with the tests. The two molecules might be isomers, *e.g.* conformational ones. A comparison of valency angles is, however, also consistent with the hypothesis that the molecules are identical.

The thermal vibration parameters of the Ge- and the Cl-atoms appear to be of little physical significance. The principal vibration amplitudes are smaller for one chlorine atom than for the germanium atom to which it is bound. For the other chlorine atoms the reverse was found. We have therefore not corrected the Ge—Cl distances for vibration effects.

In $CsGeCl_3$ Ge is coordinated to six Cl-atoms of a distorted octahedron with three short Ge—Cl bonds (2.31 Å) and three long ones (3.13 Å). Thus there is a tendency towards the formation of $GeCl_3^-$ ions of pyramidal shape. When the caesium ion is replaced by the more bulky pilocarpinium ion, the $GeCl_3^-$ groups cannot come close enough together to influence the coordination around Ge. None of the atoms in the pilocarpine molecules are within the coordination sphere of Ge. The $GeCl_3^-$ ion probably exists in HCl solutions as a well defined unit like the $SnCl_3^-$ ion. Test tube experiments have shown that $GeCl_3^-$ like $SnCl_3^-$ reacts with several Pt and Pd complexes making strongly coloured compounds.

The pilocarpine ion contains a γ-lactone ring and an imidazole ring. The planes of the rings define an angle of 87.6°. A molecule is shown in Fig. 1 in a perspective drawing. A conventional planar drawing is shown in Fig. 2 showing mean distances and angles. The imidazole ring is planar within experimental accuracy. The standard deviation for a least-squares plane through N1, N2, C7, C9, C10, and C11 is 0.027 Å with no atom more than twice this distance from the plane. We searched for hydrogen atoms in a difference Fourier map. Peaks of height 0.3 electrons/Å^3 were found at locations which

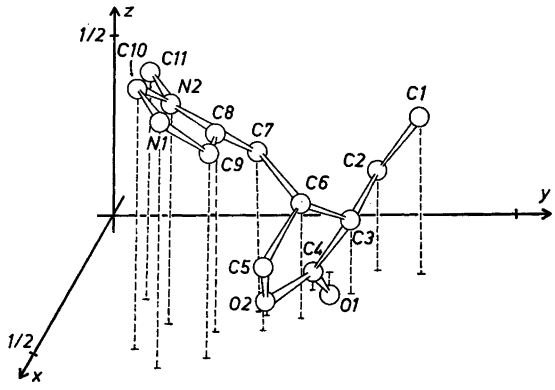

Fig. 1. Clinographic projection of a pilocarpine molecule.

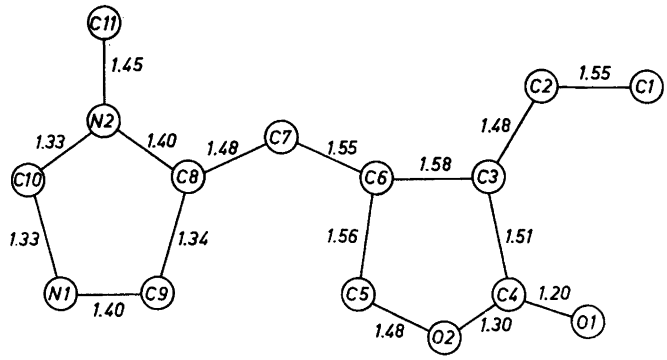

Fig. 2. Conventional planar projection of a pilocarpine molecule showing bond distances in Å units.

could reasonably be expected to be hydrogen sites but regions of positive and negative electron densities of 0.5 e/Å^3 were found at various random locations in the unit cell so we cannot with certainty locate hydrogen atoms. From naive valency considerations and from the bond distances found we suggest that a hydrogen ion is located at N1. The bond distances in the imidazole ring indicate a system of delocalized π-electrons.

Fig. 3 shows the lactone ring with the distances from a least-squares plane through C3, C4, C5, O1, and O2. The C—C distances in this part of the molecule all correspond to single bonds. The distance C4—O1 is a normal carbonyl distance. The difference between O2—C5 and O2—C4 (0.18 Å, σ=0.03 Å) is probably significant and indicates a bond order higher than one for O2—C4.

The packing of the molecules is shown in outline in Fig. 4. As a first approximation the structure may be described as ionic and composed of pilocarpinium ions and of trichlorogermanate(II) ions. Intermolecular N—O distances are found in the region 2.76—3.07 Å. Only one, $N1_2$—$O1_1$ (2.76 Å), is highly indicative of a hydrogen bond. A possible hydrogen bond scheme is shown in Fig. 5. The water molecule has vibration amplitudes so high as to suggest that it either has a site occupation factor less than one or that its

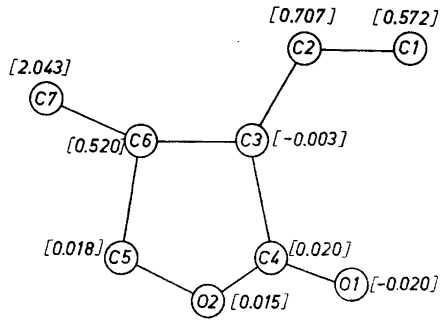

Fig. 3. The γ-lactone part of the pilocarpine molecule. The distances in Å units are given from the least squares plane through C3, C4, O1, O2, and C5.

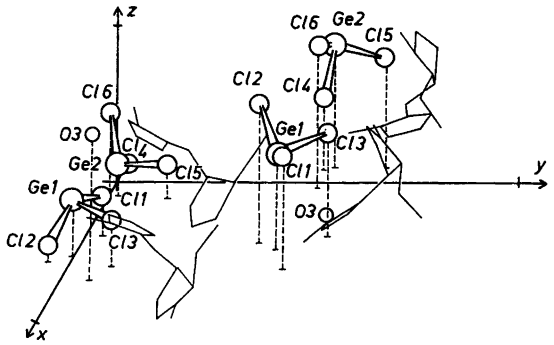

Fig. 4. Clinographic projection of a unit cell of pilocarpine-trichlorogermanate(II).

location in the unit cell is random within a certain volume. It may possibly form a hydrogen bond with Cl3 (O—Cl=3.25 Å).

Since $HGeCl_3$ forms salts with compounds as pilocarpine and quinine from HCl solutions we found it worthwhile to investigate the possibilities of compound formation with other alkaloids.

Solutions of ergotamine tartrate, papaverine chloride, methyl-atropine bromide, homatropine bromide, tropine, and tropinone yielded no precipitate

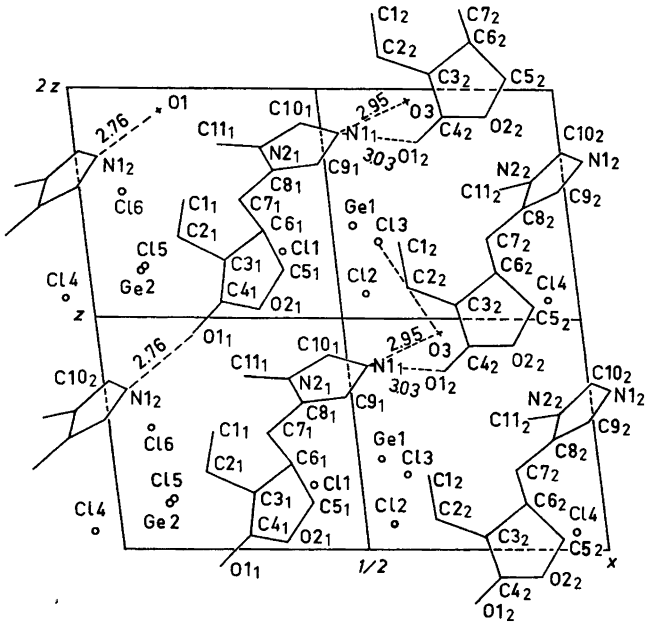

Fig. 5. xz projection of half a unit cell indicating packing and hydrogen bond scheme.

with $HGeCl_3$. Theobromine, coffeine, theophylline, cocaine chloride, strychnine phosphate, and scopolamine bromide gave crystalline precipitates with $HGeCl_3$ solutions. The scopolamine compound is at present subject to an X-ray structural investigation.

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