structural information on similar compounds is available. It is interesting to note the general similarities between the structure of the negatively charged selenium system in this crystal and the structure of the molecular adduct of selenium oxychloride and two pyridine molecules.[3] These are presently the only structures reported for five-bonded selenium, if the present structure is so classified. Both structures have square-pyrimidal arrangements (with apical oxygen atoms) about the selenium, and both have bond distances that are difficult to interpret. In the molecular compound, one of the *trans* selenium–chlorine and both of the *trans* selenium–nitrogen bonds were elongated (2.57, 2.20, and 2.19 A, respectively), while in the ion of this report the two *cis* selenium–chlorine distances were elongated. In both structures the bond angles formed by the oxygen, the selenium, and the tightly held chlorines are the largest deviations from right angles in the square-pyramidal units. In each structure there is good evidence for a very weak chlorine bridge to the open position below the base of the square pyramid.

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The Crystal and Molecular Structure of Trichlorosilyltetracarbonylcobalt, $Co(SiCl_3)(CO)_4$

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The crystal and molecular structure of trichlorosilyltetracarbonylcobalt, $Co(SiCl_3)(CO)_4$, has been determined from three-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares techniques, until the *R* factor for 664 intensities above background is 3.4%. The material crystallizes in space group C_{2h}^5-$P2_1/c$ of the monoclinic system, with four molecules in a cell of dimensions $a = 8.561$, $b = 10.888$, $c = 11.657$ A; $\beta = 99° 47'$. Molecules of $Co(SiCl_3)(CO)_4$ are well-separated in the solid state, the shortest Co···Co distance being 6.42 A. The molecules exhibit slight, but significant, deviations from C_{3v} symmetry. The configuration of the Co atom is trigonal bipyramidal; that of the Si atom is tetrahedral. The three equatorial carbonyl groups are displaced out of the equatorial plane toward the Si atom and are in a staggered conformation with respect to the Cl atoms. The Si–Co bond length is 2.254 ± 0.003 A.

Introduction

The work described here on the determination of the crystal and molecular structure of trichlorosilyltetracarbonylcobalt, $Co(SiCl_3)(CO)_4$, was undertaken for several reasons. First, there is a continuing effort in this laboratory to obtain reliable experimental information on the geometries of five-coordinate transition metal complexes.[2] Second, there is general interest in the structures of transition metal hydrides.[2] The compound $HCo(CO)_4$, owing to its instability, has not been studied by diffraction methods. Yet because it is one of the parent carbonyl hydrides there is a need for structural information. It has been found that the $Mn(CO)_5$ geometries in $(CO)_5Mn$–$Mn(CO)_5$[3] and in $HMn(CO)_5$[4] are essentially identical. Thus a knowledge of the structure of a compound of the type $XCo(CO)_4$ should provide indirect information on the structure of $HCo(CO)_4$. Third, although compounds containing the Si–M bond, where M is a transition metal, have been known for some time,[5] no structural information is available. Infrared spectral data on several silylcobalt carbonyls of general formula $R_3SiCo(CO)_4$ ($R =$ H, F, Cl, C_2H_5, C_6H_5, H_3CO)[6–8] have been interpreted in terms of multiple bonding between Si and Co. It is thus of interest to determine the structure of at least one of these compounds to provide information on the Si–Co bond length. The compound $Co(SiCl_3)(CO)_4$ was chosen because of its general stability and suitable melting point (44°).

Collection and Reduction of Intensity Data

A sample of $Co(SiCl_3)(CO)_4$, prepared according to the method of Chalk and Harrod,[6] was kindly supplied by Mr. A. P. Hagen. Crystals were grown by subliming the sample under vacuum from a break-seal tube into a 0.2-mm quartz capillary attached to the bottom of a glass trap which was immersed in liquid

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[2] J. A. Ibers, *Ann. Rev. Phys. Chem.*, **16**, 375 (1965).

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

[4] S. J. La Placa, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, **3**, 1491 (1964).

[5] T. S. Piper, D. Lemal, and G. Wilkinson, *Naturwissenschaften*, **43**, 129 (1956).

[6] A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 1133 (1965).

[7] B. J. Aylett and J. M. Campbell, *Chem. Commun.*, 217 (1965).

[8] A. P. Hagen and A. G. MacDiarmid, *Inorg. Chem.*, **6**, 686 (1967).

nitrogen. After some material was sealed into the capillary, it was again sublimed, from one end to the other, until transparent, yellow crystals were obtained which were isolated from their neighbors and were firmly attached to the capillary wall. Three such samples were examined during the preliminary precession photography. The compound was found to possess monoclinic symmetry. The systematic absences of $0k0$ for k odd and $h0l$ for l odd, observed on photographs from all crystals, are strongly indicative of the space group C_{2h}^5-$P2_1/c$. Approximate lattice constants were obtained from these photographs. The final values, and their standard deviations, as obtained from a least-squares refinement of the setting angles of fourteen reflections which had been carefully centered on a Picker four-circle automatic X-ray diffractometer, are $a = 8.561 \pm 0.004$, $b = 10.888 \pm 0.004$, $c = 11.657 \pm 0.005$ A; $\beta = 99° 47' \pm 2'$ ($t = 28°$, λ (Mo $K\alpha_1$) 0.70926 A). The formula weight is 305.45 and for four molecules in the unit cell the calculated density is 1.89 g/cm^3; this is a reasonable density, but no experimental value is available for comparison owing to the sensitivity of the compound to moist air. With four molecules in $P2_1/c$ no crystallographic symmetry conditions need be imposed on the molecule.

The procedures used in data collection and processing for the most part parallel those described previously[9,10] and only differences will be emphasized. Trial scans through several reflections from the first crystal mounted on the diffractometer showed that there were two crystals in very nearly identical orientations. This was not detectable, even in retrospect, from the preliminary precession photographs. A second crystal, used for gathering the intensity data, gave clean 2θ and ω scans, even though preliminary photographs had shown that there were reflections from randomly oriented nearby crystals. During the initial alignment, correctly indexed reflections from one such crystal were inadvertently put into the lattice parameter refinement together with correctly indexed reflections from the main crystal. The results were disastrous. Reflections with these same indices were subsequently located from the main crystal and found to be ten times more intense than those from the nearby crystal. Throughout this study we considered the possibility of random overlapping of reflections from these two crystals.

It was not possible to measure the dimensions of the main crystal accurately through the cylindrical capillary walls, especially since there was a fine deposit of microcrystallites on these walls. For the purposes of an approximate absorption correction the crystal was described as a rectangular parallelepiped of dimensions 0.30 × 0.15 × 0.15 mm. The linear absorption coefficient for this material is 25.2 cm^{-1} for Mo $K\alpha$ and 211 cm^{-1} for Cu $K\alpha$. In order to minimize problems of absorption and fluorescence Mo $K\alpha$ radiation was used in the data collection. The diffracted beams were filtered through 3.0-mil Zr foil. The pulse height analyzer was centered on the Mo $K\alpha$ peak to allow approximately 90% transmission. Attentuators of copper foil, with attentuator factors of about 2.3, were automatically inserted into the beam path when the intensity of the diffracted beam exceeded about 7000 counts/sec during the scan. The intensities were collected by the θ–2θ scan technique, using a take-off angle of 0.6° and a scan rate of 1°/min. At this take-off angle, the peak intensity of a typical reflection was about 80% of its maximum value as a function of take-off angle. The 2θ scan range from 0.4° below to 0.6° above the Mo $K\alpha_1$ peak was found to be sufficient to include the total intensity from all reflections. Stationary-crystal, stationary-counter background counts of 10 sec were taken at each end of the scan. The background counts were generally high throughout reciprocal space, presumably as a result of the scattering from the microcrystallites on the capillary walls. The defining aperture for the diffracted beams, a rectangle 7 × 7 mm, was placed 21 cm from the crystal. Standard reflections were measured at various intervals during the runs. Their constancy indicated no decomposition of the crystal in the X-ray beam.

For reasons detailed previously, we have found it highly desirable to collect complete data sets; *i.e.*, all four forms of equivalent reflections for this monoclinic crystal. Yet the general level of intensity from Mo $K\alpha$ radiation is lower than that from Cu $K\alpha$ used previously, and in order to eliminate the time necessary to collect four forms from a reflection whose intensity is below background, the following procedure was adopted. Preliminary scans indicated that there were few, if any, useful data to be collected beyond a 2θ value of 40°. Data were initially collected for the 1008 unique reflections within the range 0 to 40°. It was found on processing these data that only 740 F^2 values exceed $\sigma(F^2)$, where $\sigma(F^2)$ is the estimated standard deviation of F^2 obtained in the manner described previously.[9] (We shall subsequently refer to intensities for which $F^2 < \sigma(F^2)$ as being below background.) Accordingly the three additional forms to complete the data set were generated from these 740 reflections. Subsequent processing of the entire data set led to 644 reflections that were above background; thus 96 intensities which were above background for one form only, when averaged, decreased below background. After processing of the entire data set comparisons of the estimated standard deviations from individual measurements and from the range estimate of equivalent forms[9] enabled us to eliminate a few intensities that were incorrect owing to card punching errors. In addition, four pairs of intensities were eliminated because of overlap with reflections from the secondary crystal. These were easily detected because intensities from one Friedel pair agreed very well but were very much more intense than those recorded for the other equivalent Friedel pair.

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(9) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 187 (1967).

(10) R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

The absorption correction eventually applied[11] led to transmission factors from 1.32 to 1.46. This range is sufficiently small so that our inexact knowledge of the shape of the crystal is probably not critical. In fact, comparison of a refinement with and without absorption corrections showed no significant shifts in parameters and no significant changes in agreement factors.

Final processing of the data that had been corrected for absorption, punching errors, and overlap led to the following results: of the 740 reflections observed more than once, the average value of $\sigma(F^2)$ from equivalent forms exceeded the range estimate[9] of $\sigma(F^2)$ 427 times; the R factor for averaging (which is a measure of R_1 for an F^2 refinement) was 5.8%; the predicted weighted R factor, R_2, for an F^2 refinement is 5.0%. Because in this collection scheme some reflections were observed more than once, while others were not, the estimated standard deviations of the reflections were divided by $\sqrt{n}$, where n is the number of times a given reflection was observed through its equivalent forms.

Solution and Refinement of the Structure

Initial solution and refinement of the structure were carried out from the unique data set during the period when intensities of the equivalent forms were still being collected.

The coordinates of the cobalt atom were derived from a three-dimensional Patterson function based on the 1008 unique intensities. Least-squares refinement on F (with $\sigma(F) = 0.5\sigma(F^2)/F$) of those 740 data above background yielded values of $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and the weighted R factor or $R_2 = (\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2}$ of 52.3 and 55.0%, respectively. In all calculations of F_c, the atomic scattering factors tabulated by Ibers[12] were used for Co, Si, Cl, C, and O. The effects of anomalous dispersion of Co were included in F_c;[13] the values of f' and f'' were those given by Cromer.[14]

A difference Fourier at this stage showed peaks which represented feasible silicon and chlorine positions. The set chosen was not entirely correct and led to a value of R_1 of 46%. A second difference Fourier clearly revealed an alternative set which gave a value of R_1 of 25%. A third difference Fourier, following intermediate least-squares refinements, revealed the carbon and oxygen atoms. Refinement of the atomic positions and isotropic thermal parameters for all atoms converged satisfactorily and gave a value of R_1 of 11.9%.

At this stage refinement was commenced on the 664 reflections above background, which had been obtained from the final processing of all the measurements. The same calculational model, namely isotropic thermal parameters for all the atoms, led to values of R_1 and R_2 of 7.4 and 6.4%, respectively. In the next round of calculations individual anisotropic thermal parameters were assigned to all atoms. There are several justifications for this procedure. First, the R factors for the isotropic refinement were well above those predicted from the agreement among equivalent forms in the data processing. This suggests that the least-squares model is inappropriate. Second, the isotropic thermal parameters on the oxygen and chlorine atoms were about 8 A^2. This high value, though not unexpected since data were collected only 15° or so below the melting point of the material,[15] leads one to believe that there is considerable motion in the crystal which might more suitably be described by an anisotropic model. The complete anisotropic refinement, involving 118 variable scale, positional, and thermal parameters, reduced the values of R_1 and R_2 to 3.4 and 2.7% on F; the corresponding values on F^2 are 5.0 and 5.4%. This last value agrees well with that of 5.0% predicted from the data processing; we take this agreement as a further indication that the anisotropic refinement was justified and that refinement of the structure is complete. The estimated error in an observation of unit weight is 1.12. Thus the values assigned to $\sigma(F^2)$ are reasonable on an absolute scale. A final structure factor calculation for 1008 unique reflections based on these parameters gave R_1 and R_2 values of 8.7 and 2.9%, respectively. The agreement of the weighted R factor for the complete data set with that for reflections above background suggests that the relative weighting scheme was also reasonable.

A final difference Fourier, based on the 664 observed reflections, showed no density greater than 0.28 e/A^3, roughly 6% of the height of a carbon atom in the structure.

Table I presents the final positional and thermal parameters. The estimated standard deviations on these parameters were derived from the inverse least-squares matrix. The root-mean-square amplitudes of vibration derived from these thermal parameters are presented in Table II. The magnitudes of these quantities are reasonable. The orientations of the vibrational ellipsoids are also reasonable; an indication of these orientations is provided in Figures 1 and 2. In Table III the final values of $10F_o$ and $10F_c$ (in electrons) are listed for all reflections. Those for which $F^2 < \sigma(F^2)$ are marked with an asterisk; they were not included in the least-squares refinements. A value of F_o of 0 appears if, upon correction for background, the value of F_o^2 was equal to or less than 0. For none of the unobserved reflections did F_c^2 exceed 1.5 $\sigma(F_o^2)$. An extinction correction was not applied since the data of Table III provided no indication that one was necessary.

Description and Discussion of the Structure

The structure consists of well-separated monomeric $Cl_3Si{-}Co(CO)_4$ units, the shortest Co···Co distance

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[11] In addition to various local computer programs for the CDC 3400, local modifications of the following programs were used: Hamilton's GONO9 absorption program, Zalkin's FORDAP Fourier program, the Busing and Levy ORFLS least-squares and ORFFE error function programs, and Johnson's ORTEP thermal ellipsoid plotting program.

[12] J. A. Ibers, "International Tables for X-ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

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

[14] D. T. Cromer, *ibid.*, **18**, 17 (1965).

[15] We had originally planned to repeat the structure determination at low temperatures. However, the crystal did not remain attached to the capillary wall as the capillary was cooled. In view of the reliability achieved in the present study, the low-temperature study was abandoned.

TABLE I

POSITIONAL AND THERMAL PARAMETERS FOR $Co(SiCl_3)(CO)_4$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.22354 (12)[b]	0.46735 (10)	0.27868 (9)	0.01418 (20)	0.00836 (11)	0.00926 (11)	−0.00007 (15)	0.00276 (11)	−0.00019 (12)
Si	0.30131 (26)	0.34426 (22)	0.14346 (19)	0.01604 (42)	0.00953 (28)	0.00884 (25)	−0.00040 (29)	0.00305 (26)	−0.00042 (20)
Cl_1	0.16715 (28)	0.36338 (23)	−0.01723 (18)	0.02694 (51)	0.01808 (36)	0.00898 (26)	0.00157 (36)	0.00021 (28)	−0.00163 (23)
Cl_2	0.52806 (25)	0.37542 (21)	0.12177 (20)	0.01762 (44)	0.01690 (36)	0.01489 (28)	−0.00104 (31)	0.00756 (28)	−0.00139 (24)
Cl_3	0.29176 (27)	0.16167 (20)	0.18141 (20)	0.02891 (51)	0.00876 (27)	0.01484 (29)	0.00031 (32)	0.00704 (31)	−0.00088 (20)
C_1	0.3906 (10)	0.4098 (7)	0.3707 (6)	0.0207 (19)	0.0109 (11)	0.0062 (9)	−0.0024 (11)	0.0004 (11)	0.0001 (7)
O_1	0.5026 (7)	0.3731 (6)	0.4324 (5)	0.0242 (14)	0.0165 (9)	0.0111 (7)	0.0038 (9)	−0.0009 (8)	−0.0006 (6)
C_2	0.0407 (10)	0.3872 (8)	0.2473 (8)	0.0191 (20)	0.0106 (11)	0.0130 (11)	−0.0006 (12)	0.0047 (12)	−0.0022 (8)
O_2	−0.0761 (8)	0.3348 (6)	0.2291 (6)	0.0217 (14)	0.0191 (10)	0.0233 (10)	−0.0071 (10)	0.0057 (10)	−0.0043 (7)
C_3	0.2550 (10)	0.5899 (8)	0.1851 (7)	0.0187 (18)	0.0083 (10)	0.0118 (11)	0.0018 (11)	0.0032 (11)	0.0011 (8)
O_3	0.2749 (8)	0.6695 (6)	0.1249 (6)	0.0353 (16)	0.0105 (9)	0.0186 (9)	0.0007 (9)	0.0098 (10)	0.0040 (6)
C_4	0.1638 (10)	0.5595 (8)	0.3915 (8)	0.0169 (17)	0.0119 (13)	0.0131 (12)	0.0012 (12)	0.0024 (11)	−0.0021 (9)
O_4	0.1245 (8)	0.6134 (6)	0.4652 (6)	0.0289 (15)	0.0182 (10)	0.0151 (9)	0.0048 (9)	0.0050 (9)	−0.0059 (7)

[a] The form of the anisotropic ellipsoid is $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$. [b] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits.

TABLE II

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (A)[a]

Co	0.221 (2)	0.224 (2)	0.251 (2)
Si	0.229 (3)	0.237 (4)	0.253 (3)
Cl_1	0.238 (4)	0.309 (3)	0.344 (3)
Cl_2	0.218 (3)	0.308 (3)	0.338 (3)
Cl_3	0.227 (4)	0.286 (3)	0.342 (3)
C_1	0.202 (15)	0.243 (12)	0.291 (12)
O_1	0.250 (9)	0.290 (8)	0.346 (8)
C_2	0.236 (13)	0.255 (14)	0.308 (12)
O_2	0.242 (9)	0.340 (8)	0.415 (8)
C_3	0.215 (14)	0.260 (12)	0.286 (12)
O_3	0.228 (10)	0.317 (8)	0.391 (9)
C_4	0.237 (14)	0.259 (14)	0.311 (13)
O_4	0.232 (9)	0.330 (8)	0.387 (9)

[a] The figures provide an indication of the directions of these principal axes of vibration.

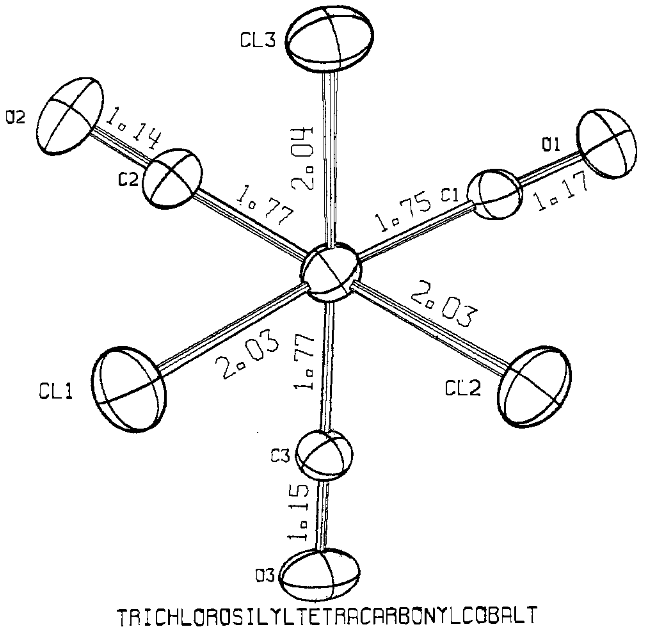

Figure 1.—One molecule of $Co(SiCl_3)(CO)_4$ viewed down the Si–Co bond.

being 6.42 A. Shortest intermolecular contacts all exceed the sums of appropriate van der Waals radii.

Selected intramolecular and intermolecular distances and angles are presented in Tables IV[16] and V.

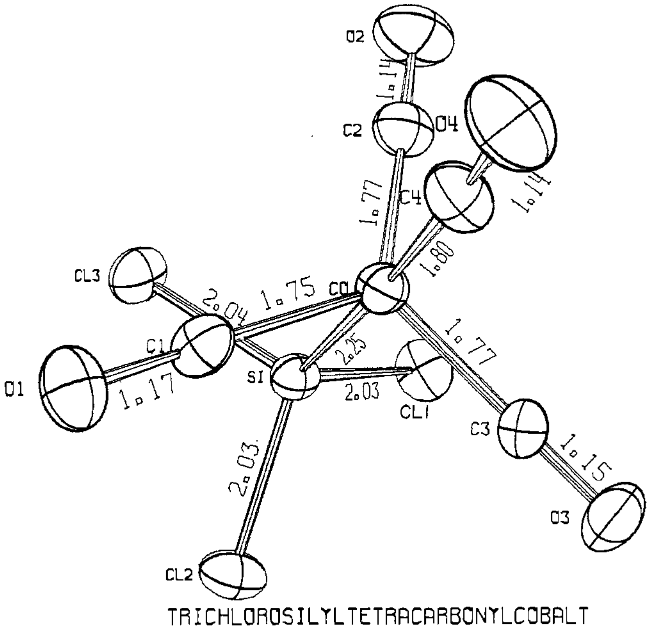

Figure 2.—Perspective drawing of $Co(SiCl_3)(CO)_4$.

Figure 1 displays the monomeric unit viewed down the Si–Co bond; Figure 2 is a perspective drawing of the unit. It is apparent from the data in these tables and from the figures that the entire molecule possesses approximate C_{3v} symmetry, in agreement with the deductions from the infrared study.[8] Statistically significant deviations from this symmetry, exemplified by the dihedral angles between the three Si, Co, $C_{1,2,3}$ planes, may be attributed to unsymmetrical molecular packing in this monoclinic structure. The C_{3v} configuration with equatorial carbonyls and chlorines staggered can be rationalized by the minimization of van der Waals repulsions between nonbonded atoms in the molecule.

The five-coordinate Co atom has a trigonal bipyramidal arrangement for its ligands; the Co is displaced 0.15 A out of the equatorial plane of the carbonyl carbon atoms toward the terminal carbonyl. This displacement is somewhat less than has been found in general for five-coordinate transition metal complexes.[2] A preliminary report[17] on the structure of

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(16) Reasonable assumptions concerning the effects of thermal motion result in changes in these bond distances that are less than 0.01 A for those involving Co and less than 0.05 A for the others; however, the trends apparent in Table IV are not changed.

(17) B. T. Kilbourn, T. L. Blundell, and H. M. Powell, *Chem. Commun.*, 444 (1965).

TABLE III

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×10) (IN ELECTRONS) FOR Co(SiCl$_3$)(CO)$_4$

K	L	OBS	CALC
**** H = 0 ****			
0	0		5935
0	2	923	933
0	4	137	126
0	6	158	140
0	8	342	345
0	10	* 83	16
1	1	111	100
1	2	638	632
1	3	304	301
1	4	483	492
1	5	420	429
1	6	288	296
1	7	735	716
1	8	* 76	104
1	9	155	156
1	10	* 82	73
1	11	104	131
2	0	486	475
2	1	760	759
2	2	566	559
2	3	139	128
2	4	510	511
2	5	* 53	93
2	6	387	388
2	7	614	611
2	8	* 67	41
2	9	113	124
2	10	82	80
3	1	760	762
3	2	* 28	46
3	3	398	405
3	4	223	232
3	5	175	171
3	6	460	458
3	7	175	141
3	8	121	129
3	9	440	425
3	10	120	92
4	0	1574	1535
4	1	607	590
4	2	582	596
4	3	398	406
4	4	448	454
4	5	190	195
4	6	354	366
4	7	* 0	8
4	8	126	144
4	9	91	72
4	10	* 0	60
5	1	* 0	46
5	2	639	658
5	3	266	268
5	4	802	818
5	5	300	314
5	6	144	158
5	7	* 51	164
5	8	153	144
5	9	144	132
6	0	753	729
6	1	229	234
6	2	345	338
6	3	561	565
6	4	* 0	8
6	5	417	429
6	6	164	160
6	7	147	157
6	8	* 49	18
6	9	* 0	27
7	1	283	262
7	2	79	13
7	3	64	22
7	4	68	58
7	5	181	157
7	6	177	165
7	7	272	283
7	8	287	282
8	0	151	129
8	1	328	311
8	2	184	180
8	3	281	267
8	4	* 62	60
8	5	150	124
8	6	* 0	26
8	7	* 22	83
9	1	* 0	4
9	2	119	87
9	3	* 0	105
9	4	* 0	19
9	5	* 67	135
10	0	321	318
10	1	342	356
10	2	* 0	132
10	3	140	165
**** H = 1 ****			
0	0	194	189
0	2	421	415
0	4	1441	1489
0	6	608	624
0	8	343	342
0	10	438	416
0	-2	188	179
0	-4	847	838
0	-6	752	756
0	-8	441	430
0	-10	385	368
1	0	884	854
1	1	1256	1296
1	2	400	399
1	3	693	690
1	4	344	347
1	5	* 65	26
1	6	506	507
1	7	242	242
1	8	* 82	14
1	9	120	106
1	10	112	91
1	-1	1148	1111
1	-2	* 0	68
1	-3	80	93
1	-4	* 0	17
1	-5	351	356
1	-6	195	194
1	-7	353	366
1	-8	125	127
1	-9	* 70	44
1	-10	* 86	60
1	-11	* 0	86
2	0	203	200
2	1	124	114
2	2	646	654
2	3	85	97
2	4	540	543
2	5	* 49	24
2	6	250	249
2	7	421	405
2	8	261	253
2	9	213	179
2	10	178	188
2	-1	546	518
2	-2	907	896
2	-3	2100	2237
2	-4	551	553
2	-5	355	365
2	-6	282	271
2	-7	444	445
2	-8	248	254
2	-9	88	112
2	-10	228	212
2	-11	65	70
3	0	503	488
3	1	849	842
3	2	371	375
3	3	544	554
3	4	470	478
3	5	786	798
3	6	70	30
3	7	* 77	75
3	8	122	119
3	9	* 0	86
3	10	* 85	60
3	-1	757	723
3	-2	313	308
3	-3	1029	1036
3	-4	223	224
3	-5	167	162
3	-6	* 72	134
3	-7	332	327
3	-8	* 0	102
3	-9	158	166
3	-10	66	63
4	0	377	371
4	1	147	151
4	2	335	334
4	3	* 0	40
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4	5	221	219
4	6	* 0	20
4	7	112	120
4	8	194	201
4	9	* 89	142
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4	-3	136	142
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4	-7	* 55	107
4	-8	261	259
4	-9	214	209
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5	2	193	204
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5	4	286	288
5	5	186	201
5	6	640	643
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5	8	* 36	101
5	9	* 0	46
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6	6	* 87	191
6	7	* 47	124
6	8	135	127
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6	-4	* 0	27
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6	-6	326	328
6	-7	148	135
6	-8	200	204
6	-9	256	264
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7	2	528	524
7	3	149	121
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7	5	107	142
7	6	* 0	75
7	7	109	56
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7	-3	164	183
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7	-5	87	97
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7	-7	160	184
7	-8	* 58	56
8	0	* 85	74
8	1	* 0	78
8	2	* 34	76
8	3	139	128
8	4	133	135
8	5	235	231
8	6	* 91	94
8	-1	75	102
8	-2	* 76	81
8	-3	248	254
8	-4	135	145
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8	-6	* 48	17
8	-7	316	344
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9	1	89	34
9	2	374	359
9	3	97	85
9	4	228	239
9	5	* 23	40
9	-1	* 91	57
9	-2	165	157
9	-3	104	72
9	-4	135	126
9	-5	* 0	7
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10	2	* 0	73
10	-1	* 59	61
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10	-3	168	148
**** H = 2 ****			
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0	-8	* 0	51
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1	-7	538	535
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2	5	104	106
2	6	405	407
2	7	214	220
2	8	149	142
2	9	* 0	27
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2	-2	744	723
2	-3	217	219
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2	-7	121	129
2	-8	* 0	147
2	-9	* 20	102
2	-10	109	124
2	-11	* 0	4
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3	3	* 50	62
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3	6	181	170
3	7	77	84
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4	6	307	296
4	7	116	122
4	8	249	230
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4	-2	481	488
4	-3	475	481
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4	-5	* 0	8
4	-6	641	650
4	-7	151	150
4	-8	107	132
4	-9	* 55	97
4	-10	* 66	19
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5	6	253	257
5	7	237	227
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5	-3	137	139
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5	-6	396	401
5	-7	232	215
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6	2	464	462
6	3	150	138
6	4	* 87	107
6	5	440	437
6	6	125	94
6	7	86	89
6	8	* 0	16
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6	-2	* 0	71
6	-3	323	326
6	-4	299	297
6	-5	116	95
6	-6	* 0	105
6	-7	* 0	53
6	-8	95	97
6	-9	* 67	93
7	0	* 32	41
7	1	* 33	73
7	2	* 29	71
7	3	80	79
7	4	* 0	32
7	5	* 0	92
7	6	163	152
7	7	* 0	68
7	-1	* 0	60
7	-2	* 0	74
7	-3	247	228
7	-4	198	180
7	-5	* 0	110
7	-6	307	303
7	-7	108	105
7	-8	272	281
8	0	215	221
8	1	326	323
8	2	137	117
8	3	324	318
8	4	* 37	63
8	5	* 79	83
8	6	* 0	37
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8	-2	* 0	19
8	-3	109	113
8	-4	196	211
8	-5	101	120
8	-6	* 0	116
8	-7	102	121
9	0	* 0	123
9	1	* 0	14
9	2	* 0	17
9	3	* 66	5
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9	-2	84	30
9	-3	78	68
9	-4	172	163
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**** H = 3 ****			
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0	8	228	216
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0	-8	603	597
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1	5	144	148
1	6	122	147
1	7	355	346
1	8	114	116
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1	-4	155	161
1	-5	108	108
1	-6	395	396
1	-7	* 0	85
1	-8	* 82	134
1	-9	* 87	26
1	-10	* 37	45
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2	2	* 49	59
2	3	63	38
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2	5	361	352
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2	7	* 72	126
2	8	167	166
2	9	233	236
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2	-2	804	795
2	-3	55	66
2	-4	459	465
2	-5	299	304
2	-6	366	373
2	-7	435	436
2	-8	259	258
2	-9	261	273
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3	1	473	487
3	2	* 0	31
3	3	457	464
3	4	209	206
3	5	614	607
3	6	309	315
3	7	* 0	24
3	8	* 0	15
3	9	* 81	91
3	-1	* 64	64
3	-2	256	255
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3	-4	100	73
3	-5	* 0	19
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4	2	* 0	102
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4	6	* 0	70
4	7	183	140
4	8	120	114
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4	-2	1341	1349
4	-3	274	271
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4	-7	268	267
4	-8	* 0	40
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5	2	* 41	32
5	3	261	269
5	4	351	361
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5	6	212	247
5	7	* 0	38
5	8	207	214
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6	1	* 0	8
6	2	* 62	57
6	3	* 0	22
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6	5	* 69	17
6	6	* 37	11
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6	-2	261	259
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6	-5	310	329
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6	-8	98	140
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7	1	* 34	3
7	2	650	647
7	3	* 0	11
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7	6	103	80
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7	-2	267	262
7	-3	157	131
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7	-5	* 0	56
7	-6	* 0	3
7	-7	* 0	99
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8	1	121	118
8	2	88	84
8	3	87	48
8	4	* 0	31
8	5	* 76	43
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8	-2	119	108
8	-3	387	356
8	-4	* 0	3
8	-5	278	269
8	-6	* 22	64
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9	1	107	126
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9	3	* 88	83
9	-1	* 38	7
9	-2	117	148
9	-3	* 66	40
9	-4	* 0	30
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0	-6	201	187
0	-8	* 0	37
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1	2	* 71	96
1	3	408	419
1	4	459	450
1	5	176	186
1	6	* 91	81
1	7	196	200
1	8	93	72
1	-1	178	183
1	-2	319	314
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2	2	330	345
2	3	153	147
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2	7	* 63	15
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2	-3	554	551
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2	-6	66	54
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3	2	* 0	5
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3	4	154	164
3	5	* 0	28
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3	7	76	17
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3	-3	209	184
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3	-5	* 0	42
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4	7	205	193
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4	-4	443	451
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4	-6	218	214
4	-7	141	150
4	-8	223	242
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5	-3	368	370
5	-4	173	179
5	-5	267	269
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5	-7	* 0	78
5	-8	* 57	95
5	-9	152	133
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6	1	207	204
6	2	327	323
6	3	256	247
6	4	* 0	73
6	5	310	314
6	6	* 52	16
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6	-2	139	169
6	-3	462	475
6	-4	272	273
6	-5	219	207
6	-6	* 21	37
6	-7	140	159
6	-8	114	136
7	0	96	116
7	1	117	105
7	2	* 81	72
7	3	155	151
7	4	* 0	74
7	5	* 0	20
7	-1	* 0	5
7	-2	306	298
7	-3	164	179
7	-4	287	290
7	-5	247	239
7	-6	251	253
7	-7	* 0	18
8	0	* 57	25
8	1	212	199
8	2	* 0	4
8	3	207	229
8	-1	177	184
8	-2	* 0	14
8	-3	* 0	40
8	-4	103	38
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9	0	* 51	58
9	1	* 76	74
9	-1	161	155
9	-2	* 51	65
**** H = 5 ****			
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0	6	89	91
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0	-4	880	880
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0	-8	330	323
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1	2	453	459
1	3	695	707
1	4	241	225
1	5	228	223
1	6	* 70	52
1	7	* 86	22
1	-1	134	149
1	-2	291	280
1	-3	* 0	17
1	-4	159	147
1	-5	287	291
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1	-7	116	110
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2	2	285	306
2	3	185	197
2	4	* 76	49
2	5	* 62	54
2	6	* 77	96
2	7	* 0	19
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2	-2	492	496
2	-3	519	520
2	-4	268	274
2	-5	258	256
2	-6	268	247
2	-7	188	172
2	-8	175	177
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3	3	104	102
3	4	240	239
3	5	261	276
3	6	157	139
3	7	293	286
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3	-3	291	288
3	-4	* 73	88
3	-5	376	374
3	-6	* 0	93
3	-7	285	285
3	-8	* 77	62
3	-9	* 50	84
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4	1	240	242
4	2	218	221
4	3	* 0	22
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4	5	* 64	14
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4	-1	237	230
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4	-3	256	249
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4	-6	343	345
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5	3	* 0	79
5	4	* 71	80
5	5	* 67	102
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5	-3	* 0	18
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5	-6	112	137
5	-7	* 0	14
5	-8	* 75	100
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6	2	92	113
6	3	* 57	44
6	4	* 66	124
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6	-2	* 0	44
6	-3	174	184
6	-4	303	301
6	-5	196	174
6	-6	194	203
6	-7	274	298
7	0	215	212
7	1	* 0	15
7	2	232	221
7	3	* 0	87
7	-1	* 0	27
7	-2	* 65	32
7	-3	* 0	75
7	-4	199	205
7	-5	176	159
8	0	* 0	40
8	1	* 57	47
8	-1	206	227
8	-2	* 81	91
8	-3	284	293
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0	6	238	215
0	-2	174	193
0	-4	228	227
0	-6	183	135
0	-8	* 90	188
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1	1	279	272
1	2	109	135
1	3	181	189
1	4	* 64	33
1	5	* 73	10
1	6	163	194
1	-1	534	530
1	-2	67	84
1	-3	349	348
1	-4	143	149
1	-5	303	293
1	-6	* 0	39
1	-7	169	150
1	-8	144	162
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2	1	* 0	25
2	2	160	142
2	3	115	121
2	4	196	182
2	5	* 91	151
2	-1	* 19	6
2	-2	156	161
2	-3	231	244
2	-4	* 0	48
2	-5	89	95
2	-6	202	207
2	-7	82	73
2	-8	198	222
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3	1	273	279
3	2	* 35	12
3	3	* 0	37
3	4	* 59	36
3	5	* 0	11
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3	-2	303	302
3	-3	257	240
3	-4	209	219
3	-5	246	234
3	-6	* 66	76
3	-7	290	299
3	-8	204	228
4	0	289	272
4	1	178	167
4	2	* 21	28
4	3	* 0	99
4	4	82	84
4	-1	* 35	76
4	-2	* 79	59
4	-3	* 54	107
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4	-5	200	194
4	-6	110	89
4	-7	* 85	103
5	0	295	310
5	1	* 0	52
5	2	193	188
5	3	126	63
5	4	* 0	40
5	-1	* 0	10
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5	-3	211	207
5	-4	151	149
5	-5	190	201
5	-6	122	141
6	0	* 0	5
6	1	221	229
6	2	207	212
6	-1	124	124
6	-2	* 0	107
6	-4	129	141
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7	0	* 0	29
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7	-2	172	169
7	-3	* 76	104
**** H = 7 ****			
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1	0	* 86	61
1	1	221	210
1	2	119	125
1	3	* 0	102
1	4	* 40	7
1	-1	* 75	97
1	-2	* 66	103
1	-3	125	108
1	-4	209	215
1	-5	173	149
1	-6	* 0	51
1	-7	135	141
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2	2	189	197
2	3	72	49
2	-1	282	270
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2	-3	* 82	72
2	-4	161	159
2	-5	262	268
2	-6	110	125
2	-7	* 0	6
3	0	73	62
3	1	* 72	37
3	2	* 67	111
3	3	219	215
3	-1	* 77	89
3	-2	* 48	30
3	-3	* 0	26
3	-4	238	222
3	-5	179	179
3	-6	* 60	53
4	0	* 0	228
4	1	150	140
4	2	* 60	87
4	-1	149	147
4	-2	214	230
4	-3	157	146
4	-4	* 59	114
4	-5	* 68	118
5	0	136	187
5	-1	* 0	42
5	-2	* 0	88
5	-3	110	89
5	-4	* 76	61
**** H = 8 ****			
0	0	* 88	32
0	-2	294	288
0	-4	197	217
1	0	146	163
1	-1	151	178
1	-2	152	134
1	-3	275	293
1	-4	174	205
2	-1	161	183
2	-2	* 0	73
2	-3	* 68	96

TABLE IV

SELECTED DISTANCES (A)

Intramolecular bonded distances

Co–Si	2.254 (3)
Co–C$_4$	1.797 (9)
Co–C$_1$	1.751 (9)
Co–C$_2$	1.775 (9)
Co–C$_3$	1.773 (9)
C$_4$–O$_4$	1.136 (8)
C$_1$–O$_1$	1.167 (8)
C$_2$–O$_2$	1.140 (9)
C$_3$–O$_3$	1.146 (8)
Si–Cl$_1$	2.035 (3)
Si–Cl$_2$	2.028 (3)
Si–Cl$_3$	2.041 (3)

Intermolecular[a] distances

Co–Co	6.42
O–O	3.07
O–Cl	3.44
Cl–Cl	3.85

Intramolecular nonbonded distances

Co–O$_4$	2.932 (6)
Co–O$_1$	2.918 (6)
Co–O$_2$	2.914 (7)
Co–O$_3$	2.918 (7)
C$_4$–C$_1$	2.578 (12)
C$_4$–C$_2$	2.618 (12)
C$_4$–C$_3$	2.674 (12)
Si–C$_1$	2.725 (8)
Si–C$_2$	2.753 (9)
Si–C$_3$	2.759 (9)
Cl$_1$–Cl$_2$	3.238 (4)
Cl$_2$–Cl$_3$	3.236 (3)
Cl$_3$–Cl$_1$	3.238 (4)
Cl$_1$–C$_2$	3.446 (9)
Cl$_1$–C$_3$	3.407 (9)
Cl$_2$–C$_3$	3.472 (9)
Cl$_2$–C$_1$	3.333 (8)
Cl$_3$–C$_1$	3.500 (8)
Cl$_3$–C$_2$	3.435 (8)

[a] The shortest intermolecular distances of the type specified.

TABLE V

SELECTED ANGLES (DEGREES)

Bond angles

Co–Si–Cl$_1$	113.29 (13)
Co–Si–Cl$_2$	112.98 (13)
Co–Si–Cl$_3$	113.58 (11)
Cl$_1$–Si–Cl$_2$	105.69 (14)
Cl$_2$–Si–Cl$_3$	105.33 (14)
Cl$_3$–Si–Cl$_1$	105.19 (14)
Si–Co–C$_1$	84.74 (26)
Si–Co–C$_2$	85.31 (27)
Si–Co–C$_3$	85.61 (27)
C$_4$–Co–C$_1$	93.19 (38)
C$_4$–Co–C$_2$	94.29 (38)
C$_4$–Co–C$_3$	97.02 (41)
C$_4$–Co–Si	177.21 (30)
Co–C$_4$–O$_4$	177.12 (90)
Co–C$_1$–O$_1$	179.05 (77)
Co–C$_2$–O$_2$	178.73 (92)
Co–C$_3$–O$_3$	179.67 (83)

Dihedral angles[a]

Co–Si–Cl$_1$ Co–Si–Cl$_2$	120.16 (20)
Co–Si–Cl$_1$ Co–Si–Cl$_3$	119.94 (19)
Co–Si–Cl$_3$ Co–Si–Cl$_2$	119.90 (20)
Si–Co–C$_1$ Si–Co–C$_2$	124.17 (38)
Si–Co–C$_2$ Si–Co–C$_3$	118.23 (41)
Si–Co–C$_3$ Si–Co–C$_1$	117.60 (38)
Si–Co–O$_1$ Si–Co–O$_2$	124.03 (20)
Si–Co–O$_2$ Si–Co–O$_3$	118.68 (20)
Si–Co–O$_3$ Si–Co–O$_1$	117.30 (18)

[a] Angles are between two planes each defined by three atoms.

$(C_6H_5)_3PAu–Co(CO)_4$ indicates a very similar Co environment in this compound. In $Cl_3Si–Co(CO)_4$ the mean axial–equatorial C–C distance is 2.62 A, essentially that found in other compounds where equatorial carbonyl groups are free to move away from axial ones (*e.g.*, $Mn_2(CO)_{10}$[3] and $HMn(CO)_5$[4]). However, shorter nonbonded distances are possible when the equatorial carbonyls are constrained by other structural features (*e.g.*, $((C_6H_5)_2P)H(Mn(CO)_4)_2$[18]).

The $Co(CO)_4$ fragment has idealized symmetry C_{3v}, but not T_d symmetry. It has been pointed out[19] that the infrared spectral data on $HCo(CO)_4$ are consistent with either of these symmetries. We believe it reasonable to assume that the structure of $HCo(CO)_4$ will contain a $Co(CO)_4$ fragment that differs very little from that found here.

The Si atom deviates slightly but significantly from a tetrahedral environment. The mean Co–Si–Cl bond angle is 113.3°, the mean Cl–Si–Cl angle is 105.4°, and the mean Cl$\cdots$Cl distance is 3.24 A. The Si–Cl distance of 2.03 A found here compares favorably with those usually found, for example with 2.01 A in hexachlorodisilane[20] and silicon tetrachloride.[21]

The Si–Co bond length of 2.254 A represents the first determination of a length for this linkage. If one takes the tetrahedral radius of Si to be 1.17 A and the single bond radius of Co to be 1.16 A,[22] then a "single" Si–Co bond length should be approximately 2.33 A. In view of the approximate nature of this estimate, the Co–Si bond in this structure could be considered a single bond. Yet the radius estimate for Co is probably too short, for "single" Co–Co bonds in a variety of compounds are longer than 2.47 A.[23] Thus a Si–Co bond length of 2.254 A could be interpreted as indicative of some multiple bond character. On the basis of an infrared study Hagen and MacDiarmid[8] have proposed that there is considerable (d → d)π bonding in this Si–Co bond. If this is the case, then it might manifest itself in differences between the Co–CO apical linkage and the Co–CO equatorial linkages. The apical Co$\cdots$O distance is possibly significantly longer than the equatorial Co$\cdots$O distances, but the general variations among Co–C and C–O distances negate this being used as an argument in favor of Si–Co multiple bonding. In short, this study does not in any way refute the conclusions of Hagen and MacDiarmid[8] concerning multiple Si–Co bonding, nor does it corroborate them. Clearly, examination of the Si–Co bond in other substituted silylcobalt carbonyls will provide valuable information on the nature of the bonding. A determination of the structure of $Co(SiF_3)(CO)_4$ is contemplated in the near future.

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The Crystal and Molecular Structure of a Perfluoropropyl Complex of Molybdenum: π-$C_5H_5Mo(CO)_3C_3F_7$

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Tricarbonyl-π-cyclopentadienylheptafluoropropylmolybdenum, π-$C_5H_5Mo(CO)_3C_3F_7$, crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 8.301 \pm 0.007$ A, $b = 15.240 \pm 0.014$ A, $c = 11.249 \pm 0.012$ A, $\beta = 106° 15' \pm 05'$, $Z = 4$. A complete three-dimensional single-crystal X-ray analysis, based on 2172 independent reflections collected with an automated diffractometer, has been completed. The molecular stereochemistry is similar to that in π-$C_5H_5Mo(CO)_3C_2H_5$, but the molybdenum–perfluoropropyl distance is 2.288 A, as compared to a metal–carbon distance of 2.397 A in the molybdenum ethyl. This structure thus provides the first direct measurement of the contraction in metal–carbon bond length which occurs on fluorinating a transition metal alkyl. The factors stabilizing transition metal fluoroalkyls are discussed, and a table of metal–alkyl and metal–fluoroalkyl bond lengths is included.

Both chemical observations and physical measurements[1,2] indicate that the metal–carbon bond strength of transition metal perfluoroalkyls is greater than that of the corresponding nonfluorinated alkyls. While this may, in part, be due to d-orbital contraction on the metal (caused by the high electronegativity of the perfluoroalkyl group), the decrease in the C–F stretching

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