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The Crystal Structure of 8-Hydroxyquinolinium Trichlorooxyselenate

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8-Hydroxyquinolinium trichlorooxyselenate, $C_9H_8NO^+SeOCl_3^-$, forms monoclinic crystals having a unit cell with symmetry $P2_1/c$ and dimensions of $a = 12.360$, $b = 14.057$, and $c = 7.224$ A and $\beta = 107.51°$. There are four molecules per unit cell. The structure consists of a selenium–oxygen–chlorine framework held in a chainlike arrangement by chlorine bridges between selenium atoms, with the organic cations distributed around these chains. The immediate environment of each selenium is a distorted square pyramid, with an apical oxygen at 1.59 A, two *cis* chlorines at about 2.2 A, and two bridging chlorines at about 3.0 A. The final R value for 2121 reflections is 0.083.

Introduction

Relatively few structural studies have been reported for selenium compounds in which the selenium forms more than four bonds. In the more numerous structural studies of selenium compounds where the selenium forms four or fewer than four bonds, lone-pair electrons on selenium consistently play an important role in the molecular geometry.[2] This is also true for the only structure reported of five-bonded selenium, $SeOCl_2 \cdot 2py$.[3] The hexachloroselenate ions, however, are usually assumed to have octahedral structures similar to hexabromoselenate[4a] and the hexahalotellurates,[4b–6] in which the lone-pair electrons appear to have become "stereochemically inert."

The compound which is the subject of this paper was formed from the reaction of selenium tetrachloride and 8-hydroxyquinoline, followed by partial hydrolysis. The crystal study was started on the assumption that the compound was an addition product of 8-hydroxyquinoline and selenium tetrachloride. The diffraction study soon showed, however, that the organic groups were not covalently bonded to the selenium atoms. Instead, another compound of highly coordinated selenium was found which involves an interesting selenium–chlorine–oxygen chainlike structure and which provides another study of the significance of lone-pair electrons in highly bonded selenium.

Experimental Section

Preparation and Properties.—Anhydrous selenium tetrachloride was prepared directly from the elements, and reagent grade 8-hydroxyquinoline was used without purification. Solutions of each of these reagents in acetonitrile (dried with Linde Molecular Sieve 4A) were combined at room temperature to produce a flocculent yellow precipitate. This precipitate was redissolved in warm acetonitrile and slowly cooled to yield suitable crystals. *Anal.* Calcd for $SeOCl_3C_9H_8NO$: Se, 22.7; Cl, 30.6; C, 31.1; H, 2.3. Found: Se, 23.1; Cl, 31.5; C, 3.16; H, 2.2; mp 118–121°.

The pale yellow crystals are needles elongated in the c direction. Exposure to air for several minutes results in decomposition of the sample as evidenced by the appearance of the reddish brown color of elemental selenium. For the X-ray work the crystals were loaded in thin-walled capillary tubes under a nitrogen atmosphere. The crystal used for the intensity data had a "radius" of 0.050 mm and a length of 0.813 mm.

X-Ray Data.—Unit cell dimensions were obtained from a least-squares treatment of measurements made on zero-layer Weissenberg photographs taken about the b and c axes. The special camera used to obtain these films had a radius of 50 mm and utilized the Straumanis method of film placement. The unit cell parameters are: $a = 12.360 \pm 0.001$ A, $b = 14.507 \pm 0.001$ A, $c = 7.224 \pm 0.001$ A, $\beta = 107.51 \pm 0.01°$, and $V = 1235$ A^3. The assumption of four molecules per unit cell gives a calculated density of 1.87 g cm^{-3}, which is comparable to values found in our laboratory for similar compounds. This assumption proved to be correct. The systematic absences of $[h0l]$ for l odd and $[0k0]$ for k odd indicated the probable space group $P2_1/c$, C_{2h}^5; this was also confirmed by the structural refinement.

Intensities were estimated visually using multiple-film equi-inclination Weissenberg photographs taken about the c axis. Layers 0–6 were obtained; the scaling of intensities from one layer to another was done on the basis of the exposure times for each layer. Short-exposure (several hours) and long-exposure (22–52 hr) multiple-film packs were obtained for each layer. The evaluation of film factors, assignment of standard deviations to each intensity estimation, statistical combination of multiple readings, assignment of standard deviation to the resulting averages, interlayer scaling, and corrections for Lorentz and polarization effects were done using the California Institute of Technology's CRYRM programs on their IBM 7094 computer. No correction was made for absorption, since μR is only 0.5 for the crystal used.

A total of 2121 reflections was recorded and used in the final refinement out of a possible 3347 within the copper sphere; 499 of the reflections used were assigned threshold values because they were too weak to be observed.

Determination of the Structure.—The positions of the selenium and chlorine atoms were obtained from analysis of a three-dimensional map of the Patterson function. An electron density map based on the phase relationships established (for 500 of the reflections of low sin θ) by the selenium and chlorine atoms led to the location of the carbons, nitrogen, and oxygen of the planar organic cation. At this point, using isotropic temperature factors of 4.0 for each atom, a least-squares refinement produced an R factor $(= \Sigma(||F_o| - |F_c||)/\Sigma|F_o|)$ of 0.22. A three-dimensional electron density map based on the phases established for all the reflections by these atoms showed the organic molecule was not attached to the selenium and showed the oxygen bonded to the selenium. When this oxygen atom was included and two cycles of least-squares refinement were done allowing anisotropic temperature factors for the selenium and chlorine atoms, the R dropped to 0.092. A difference Fourier at this time gave positive peaks in every position expected for hydrogen atoms. The

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(1) Contribution No. 3486 from the Gates and Crellin Laboratories.

(2) S. C. Abrahams, *Quart. Rev.* (London), **10**, 407 (1956).

(3) I. Lindquist and G. Nahringbauer, *Acta Cryst.*, **12**, 638 (1959).

(4) (a) J. L. Hoard and B. N. Dickenson, *Z. Krist.*, **84**, 436 (1933); (b) E. E. Aynsley and A. C. Hazell, *Chem. Ind.* (London), 611 (1963).

(5) I. D. Brown, *Can. J. Chem.*, **42**, 2758 (1964).

(6) A. C. Hazell, *Acta Chem. Scand.*, **20**, 165 (1966).

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

0 K 0		
0	---*	6810
5 K 1		
12	183	-194
13	200	-208
14	111	123
15	63	71
16	-79	57
6 K 1		
1	144	147
2	451	482
3	87	-99
4	64	-54
5	269	-266
6	109	97
7	114	122
8	324	324
9	-94	-42
10	-96	-21
11	55	-93
12	196	-203
13	182	175
14	-94	35
15	-86	-11
7 K 1		
1	220	227
2	252	-247
3	228	-217
4	140	-122
5	134	120
6	134	141
7	78	98
8	95	-106
9	239	-264
10	-96	50
11	-94	-45
12	157	158
13	-95	93
14	60	-65
8 K 1		
1	349	-365
2	91	-97
3	222	231
4	237	225
5	-93	0
6	54	85
7	110	-108
8	124	-128
9	225	253
10	-93	24
11	73	60
12	-95	-13
13	113	-98
9 K 1		
1	152	-128
2	483	499
3	181	179
4	234	-231
5	78	-77
6	78	73
7	-96	-73
8	210	212
9	-95	-12
10	168	-156
11	-94	-11
12	60	-45
10 K 1		
1	176	161
2	-96	-76
3	383	-418
4	55	-85
5	167	134
6	144	-133
7	215	225
8	-96	3
9	241	-243
10	-93	34
11	81	102
11 K 1		
1	-94	49
2	246	-261
3	107	-84
4	263	281
5	-95	-41
6	-96	3
7	-95	63
8	157	-175
9	-89	-2
10	106	94
12 K 1		
1	-96	-41
2	-96	-61
3	201	193
4	-95	12
5	-94	-72
6	-92	21
7	109	-128
8	-79	-22
9	86	74
13 K 1		
1	-91	-58
2	-90	40
3	-87	39
4	-84	-62
5	-79	-8
6	68	-76
14 K 1		
1	-68	29
2	62	82
-15 K 2		
0	-70	-8
1	57	59
-14 K 2		
0	272	247
1	-88	25
2	71	-73
3	-85	3
4	67	-78
5	52	46
6	122	115
-13 K 2		
0	67	-75
1	176	-176
2	82	95
3	-91	-55
4	-91	29
5	185	195
6	60	-90
7	146	-147
8	-78	14
-12 K 2		
0	544	-562
1	71	88
2	158	150
3	-87	-7
4	172	163
5	-90	-24
6	224	-225
7	96	107
8	150	151
9	-85	-2
10	148	118
-11 K 2		
0	124	111
1	287	221
2	-88	-24
3	88	76
4	-88	-30
5	226	-222
6	71	76
7	171	165
8	68	-74
9	65	61
10	-89	-50
11	229	-181
12	-71	6
-10 K 2		
0	184	189
1	-85	-33
2	98	-93
3	70	-73
4	226	-226
5	72	-68
6	215	223
7	51	-53
8	50	63
9	-89	1
10	172	-182
11	44	51
12	159	116
13	97	81
-9 K 2		
0	-79	-5
1	158	-161
2	80	-89
3	-81	67
4	118	-123
5	326	318
6	99	85
7	51	-50
8	51	-56
9	88	-93
10	123	105
11	127	122
12	63	63
13	56	-48
14	83	-60
-8 K 2		
0	-72	-15
1	208	-216
2	147	166
3	182	169
4	-77	36
5	150	-136
6	302	-302
7	196	-186
8	201	-191
9	72	81
10	203	196
11	-88	-62
12	-91	-24
13	44	-66
14	39	-50
15	104	95
-7 K 2		
0	92	-81
1	180	226
2	197	-200
3	-68	-3
4	-71	-24
5	592	-594
6	154	154
7	132	146
8	180	171
9	-87	83
10	102	-90
11	203	-194
12	111	104
13	66	67
14	-89	19
15	136	94
-6 K 2		
0	697	772
1	454	-530
2	308	-347
3	-62	6
4	-65	-17
5	555	554
6	509	498
7	158	-158
8	185	-189
9	-84	-30
10	248	-242
11	72	76
12	-88	77
13	169	-163
14	-91	1
15	99	-73
16	108	-77
-5 K 2		
0	799	-913
1	750	-871
2	434	540
3	346	-343
4	592	584
5	428	408
6	706	-721
7	549	-525
8	153	159
9	140	-120
10	165	169
11	353	365
12	371	-397
13	-88	-42
14	116	128
15	-89	-37
16	151	108
-4 K 2		
0	729	-854
1	702	911
2	-46	22
3	69	84
4	544	533
5	749	-767
6	345	-348
7	555	580
8	268	266
9	64	-70
10	375	374
11	302	-312
12	306	-288
13	203	209
14	-90	-28
15	-90	3
16	129	100
-3 K 2		
0	2258*	3193
1	919	997
2	453	-371
3	417	374
4	476	-451
5	484	-493
6	567	583
7	433	423
8	545	-557
9	176	189
10	337	-347
11	378	-396
12	253	266
13	113	114
14	102	-108
15	102	96
16	91	-76
17	186	-149
-2 K 2		
1	736*	687
2	241	-235
3	388	-365
4	559	-570
5	249	271
6	447	476
7	63	-91
8	-69	4
9	196	-196
10	296	-292
11	351	382
12	290	297
13	72	90
14	-89	-23
15	93	-101
16	227	-199
17	115	98
-1 K 2		
2	181	-171
3	31	39
4	175	188
5	899	982
6	-57	-68
7	-63	8
8	40	-24
9	96	-98
10	372	392
11	278	274
12	-87	-60
13	254	-260
14	141	-122
15	172	-151
16	118	115
17	159	134
0 K 2		
1	453	-343
2	663	586
3	122	-114
4	529	504
5	133	-146
6	606	-665
7	73	-28
8	80	-69
9	360	379
10	81	85
11	98	-96
12	230	-240
13	126	-130
14	-89	45
15	211	188
16	170	142
17	110	-79
1 K 2		
0	758	-603
1	714	659
2	402	-396
3	331	-305
4	213	-227
5	415	-419
6	511	541
7	282	297
8	332	334
9	-76	6
10	287	-303
11	70	-81
12	169	183
13	135	120
14	102	98
15	65	63
16	184	-156
17	81	-52
2 K 2		
0	121	118
1	561	-551
2	99	-96
3	174	170
4	518	-514
5	941	1000
6	194	195
7	267	-280
8	94	-93
9	128	-116
10	96	-118
11	179	188
12	170	150
13	151	-152
14	85	93
15	183	-135
16	-83	10
3 K 2		
0	1070	1081
1	92	-87
2	841	800
3	55	-59
4	113	132
5	327	-307
6	923	-935
7	203	-197
8	197	211
9	206	-195
10	314	317
11	101	95
12	267	-292
13	166	165
14	94	92
15	-89	-26
16	185	144
4 K 2		
0	203	-202
1	889	885
2	157	-151
3	218	232
4	-65	1
5	916	-934
6	-72	57
7	504	492
8	145	129
9	69	-50
10	189	185
11	405	-442
12	-88	28
13	178	181
14	91	-103
15	70	49
5 K 2		
0	1118	1113
1	151	-142
2	220	-215
3	79	82
4	342	-362
5	-74	-46
6	509	525
7	-81	28
8	240	-252
9	203	221
10	343	-367
11	152	-131
12	261	261
13	66	-73
14	-89	-41
15	-78	14
6 K 2		
0	59	-30
1	560	-552
2	60	-71
3	289	-287
4	-77	-14
5	217	224
6	203	198
7	325	-313
8	-87	32
9	113	-119
10	113	-87
11	299	303
12	47	46
13	-90	-30
14	-82	-2
7 K 2		
0	381	-403
1	370	-367
2	-80	54
3	94	106
4	307	316
5	279	277
6	210	-191
7	169	-171
8	-88	-6
9	-88	-10
10	212	202
11	47	41
12	176	-142
13	181	-143
8 K 2		
0	139	128
1	109	109
2	181	180
3	100	97
4	175	160
5	189	-192
6	231	-237
7	-88	56
8	-87	-31
9	146	136
10	-91	-29
11	109	-105
12	153	-108
9 K 2		
0	220	238
1	252	260
2	170	-169
3	-88	-6
4	116	-129
5	88	-85
6	183	188
7	102	87
8	-91	54
9	79	-78
10	85	-60
11	-81	-15
12	66	68
10 K 2		
0	-87	6
1	115	-105
2	-87	6
3	-88	20
4	-89	-25
5	208	209
6	-91	-27
7	-91	-42
8	-89	-1
9	-85	-15
10	-76	17
11	-65	55
11 K 2		
0	152	-145
1	70	65
2	94	96
3	46	-60
4	90	97
5	96	-107
6	175	-154
7	56	61
8	-77	14
12 K 2		
0	41	44
1	122	125
2	97	-95
3	-84	1
4	-81	-26
5	85	-72
6	102	107
-13 K 3		
2	74	67
3	97	104
4	-86	-10
5	-84	-14
6	-81	12
7	51	-62
8	47	50
-12 K 3		
1	152	151
2	168	168
3	156	-166
4	139	-136
5	76	80
6	-86	-27
7	58	54
8	95	78
9	168	-150
10	56	-58
-11 K 3		
1	79	48
2	249	-268
3	212	-212
4	246	269
5	-80	68
6	-83	-33
7	144	143
8	220	-204
9	-85	-31
10	159	150
-10 K 3		
1	177	-166
2	109	-86
3	478	486
4	244	244
5	167	-179
6	122	115
7	165	-169
8	197	-201
9	269	253
10	84	93
11	188	-154
12	-74	22
-9 K 3		
1	71	-63
2	167	166
3	259	242
4	308	-298
5	-76	-30
6	64	-70
7	228	-232
8	208	218
9	91	102
10	44	38
11	42	44
12	93	-77
13	146	-131
-8 K 3		
1	-65	14
2	317	299
3	390	-366
4	231	-228
5	-72	3
6	43	49
7	240	235
8	309	326
9	137	-124
10	91	-98
11	139	142
12	112	-114
13	115	104
14	117	104
-7 K 3		
1	315	286
2	-60	-9
3	360	-355
4	64	-36
5	140	113
6	269	259
7	153	139
8	115	-117
9	363	-384
10	165	-164
11	-82	58
12	166	168
13	110	111
14	133	-93
15	70	-51
-6 K 3		
1	243	-251
2	681	-601
3	56	58
4	287	290
5	134	131
6	76	-89
7	121	-121
8	300	-297
9	77	102
10	182	186
11	137	124
12	90	92
13	177	-163
14	-84	-31
15	80	47
-5 K 3		
1	480	-428
2	852	748
3	259	230
4	-54	9
5	238	-221
6	-62	-2
7	77	45
8	209	221
9	222	219
10	161	-157
11	-79	-13
12	152	-148
13	62	-77
14	92	70
15	82	74
-4 K 3		
1	557	445
2	115	113
3	790	-691
4	285	-245
5	97	98
6	369	-357
7	321	311
8	105	88
9	460	-471
10	-76	-47
11	-79	32
12	-79	18
13	153	156
14	-86	-6
15	54	-49
16	56	49
-3 K 3		
1	70	-52
2	1408	1264
3	-40	30
4	565	541
5	131	-119
6	281	-275
7	-61	36
8	478	-491
9	262	259
10	311	320
11	-78	-22
12	122	111
13	90	77
14	284	-255
15	39	-44
16	141	121
-2 K 3		
1	174	-241
2	433	349
3	1319	1264
4	140	-126
5	348	-364
6	404	384
7	680	-690
8	-65	39
9	546	536
10	194	-220
11	157	-161
12	46	68
13	185	-193
14	104	-114
15	178	154
16	76	-56
-1 K 3		
2	532	488
3	64	71
4	1001	-962
5	265	256
6	266	-264
7	147	-139
8	553	594
9	108	-98
10	292	-295
11	-78	1
12	79	-77
13	91	-68
14	326	337
15	-84	11
16	84	-78
0 K 3		
1	205	167
2	572	465
3	857	-744
4	195	-179
5	318	310
6	-56	41
7	607	622
8	154	155
9	236	-272
10	267	-295
11	64	-74
12	-79	-13
13	258	268
14	121	101
15	231	-208
16	47	-45
1 K 3		
1	607	539
2	286	-253
3	111	-100
4	514	496
5	278	257
6	334	327
7	-64	-5
8	434	-468
9	280	-301
10	153	166
11	182	-174
12	184	198
13	-84	42
14	219	-209
15	93	-68
2 K 3		
1	254	-278
2	750	-644
3	535	508
4	484	444
5	152	-144
6	178	-175
7	287	-286
8	235	-243
9	360	384
10	530	532
11	-79	5
12	91	-93
13	182	-192
14	-86	0
15	63	62
16	96	92
3 K 3		
1	86	-94
2	697	662
3	-56	-20
4	114	-120
5	290	-295
6	54	68
7	41	-34
8	321	337
9	148	129
10	64	-45
11	112	114
12	230	-215
13	43	31
14	68	65
15	34	12
4 K 3		
1	415	379
2	157	-144
3	427	-409
4	-65	-30
5	117	77
6	-71	15
7	136	133
8	-77	-3
9	362	-381
10	65	77
11	45	11
12	-85	12
13	172	136
14	-78	-18
15	54	-42
5 K 3		
1	394	-377
2	427	-432
3	251	243
4	269	249
5	111	-109
6	75	82
7	-77	44
8	246	-236
9	237	253
10	91	84
11	-85	-41
12	-86	49
13	-81	-26
14	58	-49
6 K 3		
1	298	-291
2	403	410
3	321	327
4	159	-153
5	89	-86
6	156	153
7	173	-182
8	146	150
9	152	143
10	186	-199
11	-86	10
12	-82	-5
7 K 3		
1	77	63
2	133	123
3	202	-202
4	260	-259
5	112	96
6	208	-222
7	122	129
8	189	177
9	204	-190
10	59	-65
11	39	48
12	35	-35
8 K 3		
1	165	166
2	46	-76
3	326	-326
4	79	84
5	-81	59
6	-83	-51
7	225	190
8	74	-67
9	158	-121
10	-80	-24
11	75	66
9 K 3		
1	111	109
2	182	-173
3	-84	12
4	207	185
5	-86	15
6	-86	52
7	90	-107
8	150	-140
9	-75	-32
10	124	89
10 K 3		
1	121	-117
2	60	-72
3	168	177
4	-85	-11
5	56	-56
6	75	-79
7	86	-77
8	32	11
9	98	125
11 K 3		
1	-79	4
2	166	144
3	-76	-17
4	77	-82
5	-70	13
12 K 3		
1	51	46
-15 K 4		
0	124	-142
1	50	-55
2	-60	31
3	-57	-11
4	-52	28
-14 K 4		
0	83	-100
1	-78	-22
2	-77	38
3	61	41
4	-72	45
-13 K 4		
0	60	53
1	120	104
2	-89	2
3	-87	-29
4	-85	-47
5	164	-148
6	-78	27
7	77	67
-12 K 4		
0	135	128
1	64	-57
2	110	-111
3	-91	-24
4	88	-90
5	74	80
6	164	143
7	-85	-21
8	53	-42
9	-73	-27
-11 K 4		
0	79	-81
1	130	-113
2	102	93
3	65	79
4	79	72
5	-89	52
6	161	-162
7	75	-77
8	59	-50
9	56	-33
10	89	81
11	-68	8
12	-55	-30
-10 K 4		
0	-77	28
1	255	247
2	90	-79
3	-78	-21
4	79	73
5	297	-343
6	-86	3
7	142	142
8	-91	-14
9	-91	-11
10	57	47
11	138	-113
12	-69	19
13	100	88
-9 K 4		
0	452	441
1	126	-118
2	228	-224
3	-75	31
4	114	-91
5	155	153
6	305	321
7	65	-49
8	79	-70
9	100	93
10	170	-136
11	41	-39
12	105	90
13	96	-79
14	-53	-26
-8 K 4		
0	-67	-9
1	428	-409
2	177	153
3	190	-197
4	-72	48
5	350	364
6	147	-131
7	225	-224
8	65	36
9	91	-73
10	78	-68
11	268	252
12	90	-92
13	103	-93
14	95	77
-7 K 4		
0	507	-504
1	-60	15
2	50	50
3	82	-79
4	291	280
5	-69	-4
6	265	-248
7	-75	5
8	119	109
9	65	-66
10	246	255
11	100	90
12	207	-182
13	-82	-2
14	-72	-11
15	-57	-27
-6 K 4		
0	248	187
1	656	577
2	163	153
3	253	235
4	123	116
5	301	-289
6	193	-184
7	268	265
8	-76	-3
9	148	138
10	-83	-22
11	289	-277
12	76	-74
13	58	55
14	-77	18
15	96	70
-5 K 4		
0	595	575
1	867	817
2	68	-75
3	133	-115
4	367	-343
5	316	-314
6	281	279
7	316	298
8	42	-61
9	133	-106
10	236	-239
11	-87	-29
12	181	188
13	231	213
14	-81	17
15	-70	-33
16	137	-116
-4 K 4		
0	433	-403
1	406	-326
2	226	-221
3	-46	35
4	207	-200
5	574	579
6	288	268
7	172	-173
8	-72	2
9	97	-102
10	91	84
11	197	208
12	141	141
13	123	-107
14	79	-70
15	132	-94
16	-57	-19
-3 K 4		
0	553	-654
1	378	-385
2	368	418
3	76	-70
4	302	252
5	105	103
6	532	-519
7	-66	-36
8	-70	9
9	87	95
10	135	125
11	-83	13
12	148	-136
13	117	-107
14	-85	2
15	-75	20
16	127	108
-2 K 4		
1	266	297
2	223	-223
3	217	-215
4	116	-114
5	523	-515
6	292	280
7	202	196
8	-70	-3
9	129	119
10	78	-52
11	153	-138
12	114	111
13	124	81
14	-85	-42
15	132	98
16	-61	-11
-1 K 4		
0	132	134
1	460	-454
2	198	-183
3	221	204
4	416	-392
5	497	497
6	377	368
7	270	-258
8	-71	44
9	86	78
10	211	-221
11	-83	22
12	174	166
13	189	-168
14	108	87
15	-75	1
16	129	-75
0 K 4		
0	438	-403
1	404	-366
2	498	435
3	-47	-5
4	60	61
5	140	129
6	466	-463
7	278	-276
8	83	81
9	219	-228
10	78	71
11	207	210
12	163	-174
13	-91	23
14	138	114
15	112	-86
16	77	67
1 K 4		
0	634	-540
1	257	252
2	85	61
3	171	173
4	373	338
5	452	-467
6	299	-294
7	57	34
8	149	152
9	89	-90
10	297	315
11	143	-148
12	183	-183
13	119	115
14	54	-60
15	46	38
16	88	66
2 K 4		
0	405	372
1	410	376
2	32	44
3	170	164
4	-62	4
5	321	-340
6	-69	30
7	285	301
8	-76	-25
9	193	195
10	150	-151
11	340	-312
12	75	37
13	-86	50
14	-77	4
15	43	38
3 K 4		
0	697	681
1	100	-98
2	257	-237
3	279	-273
4	225	-242
5	70	-73
6	409	424
7	-76	22
8	157	-170
9	-82	-32
10	194	-177
11	109	113
12	194	175
13	67	69
14	47	-40
15	46	-44
4 K 4		
0	130	-107
1	548	-521
2	127	-112
3	-70	-4
4	131	112
5	422	429
6	62	55
7	246	-271
8	-82	-19
9	-87	-45
10	120	102
11	185	159
12	-84	-10
13	182	-153
14	67	-52
5 K 4		
1	73	60
2	192	190
3	61	54
4	222	232
5	-78	-8
6	280	-279
7	65	70
8	-88	-50
9	77	73
10	-91	32
11	-85	-38
12	171	-128
6 K 4		
1	300	297
2	162	-151
3	-78	15
4	79	-72
5	153	-143
6	165	159
7	78	62
8	-92	-5
9	74	8
10	-85	-30
11	-77	-37
12	-68	41
13	110	70
7 k 4		
2	-85	-6
3	79	62
4	102	-89
5	197	211
6	-92	20
7	61	-72
8	72	84
9	-83	-16
10	50	-41
11	44	46
8 K 4		
4	87	71
5	-90	-13
6	206	-180
7	-84	21
8	-78	5
-15 K 5		
1	-47	34
-14 K 5		
1	-65	21
2	-63	-29
3	83	-83
4	-58	28
5	-54	23
-13 K 5		
1	-75	-9
2	61	-71
3	-73	8
4	89	98
5	-68	11
6	43	51
7	-58	11
8	102	-100
-12 K 5		
1	55	-49
2	86	-101
3	150	150
4	65	69
5	-77	-32
6	-74	-23
7	113	-106
8	43	-42
9	47	49
10	87	90
-11 K 5		
1	69	-85
2	156	159
3	56	56
4	150	-163
5	78	-93
6	-81	2
7	-78	7
8	155	151
9	56	62
10	71	-72
11	41	35
-10 K 5		
1	139	149
2	132	133
3	187	-222
4	97	-94
5	57	40
6	56	67
7	87	87
8	65	58
9	156	-146
10	152	-147
11	-62	36
12	54	42
-9 K 5		
1	-69	-28
2	266	-273
3	-73	42
4	120	124
5	-80	-3
6	-83	-30
7	-85	10
8	125	-140
9	-81	9
10	51	51
11	-70	-35
12	71	70
13	-49	-7
-8 K 5		
1	205	-211
2	232	213
3	156	140
4	78	-87
5	-72	-13
6	39	41
7	40	-39
8	69	84
9	124	134
10	76	-86
11	-75	15
12	-68	9
13	83	-79
14	-42	0
-7 K 5		
1	137	145
2	191	183
3	220	-217
4	107	-84
5	122	114
6	165	-180
7	68	54
8	145	138
9	161	-194
10	55	-34
11	-79	39
12	60	-74
13	-65	35
14	55	38
-6 K 5		
1	132	120
2	415	-388
3	178	-162
4	124	123
5	-60	16
6	140	-161
7	116	131
8	139	-163
9	-83	-41
10	127	133
11	-82	-44
12	-76	39
13	153	138
14	61	-71
-5 K 5		
1	-41	49
2	196	-190
3	251	224
4	262	270
5	46	-44
6	227	235
7	226	-226
8	240	-245
9	165	164
10	-85	94
11	-83	-21
12	64	66
13	48	-50
14	157	-140
15	-47	11
-4 K 5		
1	162	-153
2	-38	37
3	479	523
4	119	-112
5	152	-167
6	48	-38
7	246	-277
8	116	108
9	174	216
10	-85	-1
11	79	-103
12	65	-57
13	130	-110
14	101	109
15	103	105
-3 K 5		
1	76	-105
2	411	487
3	106	-106
4	468	-491
5	-53	21
6	-58	-9
7	207	216
8	295	344
9	-77	45
10	250	-288
11	79	-78
12	-81	-41
13	70	67
14	162	163
15	-53	-29
-2 K 5		
1	321	331
2	39	23
3	407	-394
4	167	169
5	220	240
6	143	154
7	164	179
8	101	-89
9	284	-307
10	40	33
11	36	-47
12	-80	20
13	78	85
14	69	-51
15	78	-78
-1 K 5		
1	105	-113
2	467	-441
3	235	220
4	291	298
5	63	-57
6	-59	-18
7	82	-83
8	226	-248
9	69	57
10	281	327
11	-84	-11
12	-80	27
13	60	-49
14	52	-48
15	-51	17
0 K 5		
1	141	-156
2	340	320
3	40	-47
4	82	-53
5	57	-60
6	-61	33
7	84	-89
8	123	125
9	97	84
10	-85	-32
11	192	227
12	64	-86
13	58	-75
14	-62	29
15	-46	11
1 K 5		
1	247	241
2	67	71
3	253	-253
4	-57	15
5	-61	4
6	74	-94
7	-72	50
8	68	73
9	203	-238
10	-84	3
11	54	66
12	72	-76
13	91	76
14	38	33
15	-38	-28
2 K 5		
1	80	-81
2	343	-330
3	-59	1
4	87	93
5	52	-61
6	-71	8
7	134	139
8	155	-164
9	-85	51
10	68	57
11	52	-57
12	68	62
13	52	51
14	48	-47
3 K 5		
1	219	-214
2	-63	-32
3	201	206
4	115	116
5	55	-46
6	129	126
7	128	-118
8	69	-55
9	181	165
10	-80	-40
11	-75	8
12	-67	15
13	111	-110
4 K 5		
1	122	-109
2	133	125
3	194	204
4	216	-219
5	-81	-55
6	141	-145
7	56	-62
8	168	168
9	38	35
10	62	-79
11	56	-55
12	-60	-20
13	58	-46
5 K 5		
1	121	122
2	165	160
3	232	-262
4	172	-190
5	80	105
6	56	-82
7	149	143
8	118	109
9	107	-101
10	134	-133
11	-61	42
12	-49	12
6 K 5		
1	171	197
2	89	-84
3	151	-164
4	182	178
5	67	82
6	53	52
7	-77	-11
8	121	-110
9	115	-117
10	40	47
11	39	34
7 K 5		
1	68	-66
2	141	-113
3	164	142
4	-78	37
5	-76	-45
6	-73	-14
7	72	-73
8	66	-66
9	74	78
10	58	62
8 K 5		
1	49	-30
2	99	84
3	-72	5
4	57	-55
5	-66	14
6	-62	-2
-14 K 6		
0	30	-34
1	29	-16
2	28	24
3	-40	17
4	-35	21
-13 K 6		
0	-55	1
1	64	72
2	-54	-20
3	-53	-13
4	53	53
5	70	-82
6	28	-23
-12 K 6		
0	59	68
1	41	41
2	41	-46
3	-60	6
4	-59	-8
5	-56	-15
6	50	60
7	-49	17
-11 K 6		
0	136	154
1	-66	-44
2	-65	-16
3	53	-61
4	74	-76
5	66	87
6	86	77
7	-57	-15
8	-52	-29
9	-46	-12
10	57	-65
-10 K 6		
0	70	-64
1	141	-173
2	-66	-7
3	-66	-49
4	-66	16
5	141	133
6	-64	-22
7	134	-121
8	-59	1
9	-54	-17
10	55	56
11	99	113
-9 K 6		
0	238	-245
1	104	117
2	129	144
3	55	66
4	122	126
5	44	-32
6	203	-207
7	43	42
8	59	80
9	39	27
10	57	47
11	54	-54
-8 K 6		
0	99	93
1	373	349
2	-62	22
3	-63	-3
4	68	-53
5	179	-201
6	-66	37
7	167	164
8	-65	-29
9	-63	-6
10	68	-58
11	109	-86
12	30	23
-7 K 6		
0	137	-137
1	95	-107
2	48	-61
3	-59	30
4	122	-132
5	134	133
6	123	136
7	67	-72
8	44	58
9	-65	-23
10	41	-36
11	60	42
12	85	68
-6 K 6		
0	186	-205
1	186	-183
2	152	114
3	-54	-18
4	76	53
5	101	84
6	140	-142
7	-66	-6
8	-66	14
9	44	-44
10	42	41
11	40	29
12	35	-31
13	29	-23
-5 K 6		
0	113	132
1	62	23
2	70	-52
3	75	-79
4	-54	16
5	211	-216
6	-62	30
7	53	43
8	77	-89
9	70	75
10	61	55
11	81	-64
12	-55	25
13	31	34
-4 K 6		
1	36	-27
2	97	-96
3	94	94
4	171	-160
5	-57	21
6	184	178
7	-64	-80
8	44	33
9	100	91
10	98	-98
11	89	-75
12	98	92
13	32	-46
-3 K 6		
1	187	-217
2	-33	4
3	29	23
4	92	-78
5	148	148
6	50	46
7	134	-136
8	62	-64
9	91	-93
10	55	-63
11	133	109
12	-57	12
13	-49	-39
-2 K 6		
0	338	-307
1	211	-199
2	60	62
3	57	43
4	227	246
5	60	29
6	190	-203
7	188	-208
8	85	90
9	54	-66
10	157	147
11	90	83
12	148	-140
13	-48	-10
-1 K 6		
0	192	-180
1	330	293
2	130	126
3	82	86
4	183	205
5	160	-175
6	201	-212
7	175	191
8	92	90
9	62	62
10	-64	32
11	165	-156
12	100	-113
13	38	47
0 K 6		
0	465	442
1	179	159
2	131	-117
3	117	-110
4	148	-144
5	153	-162
6	207	196
7	122	145
8	107	-131
9	-66	51
10	83	-82
11	39	-40
12	96	85
13	67	72
1 K 6		
0	59	75
1	231	-210
2	106	-104
3	49	-54
4	60	-78
5	168	178
6	116	118
7	107	-104
8	-66	7
9	-64	-45
10	-61	-4
11	108	90
12	51	62
13	46	-46
2 K 6		
0	-62	5
1	-62	8
2	80	63
3	-64	0
4	105	105
5	81	93
6	107	-101
7	44	51
8	43	-60
9	-62	-20
10	39	31
11	35	18
12	45	-40
3 K 6		
0	63	48
1	158	151
2	44	-49
3	-66	5
4	-66	4
5	94	-82
6	44	46
7	-64	23
8	41	-35
9	39	48
10	-53	10
11	31	-29
4 K 6		
0	85	-110
1	44	42
2	-66	-27
3	44	54
4	91	-86
5	53	67
6	60	67
7	-61	-29
8	67	80
9	-53	-4
10	53	-51
5 K 6		
0	-65	-31
1	140	-117
2	53	58
3	-64	-33
4	-63	-2
5	91	75
6	62	-57
7	45	-56
8	-51	-12
9	36	-21
6 K 6		
0	167	-140
1	-61	-15
2	49	52
3	-59	-20
4	77	60
5	37	-33
6	108	-104
7	-47	-14
8	33	39
7 K 6		
1	123	115
2	-53	5
3	-51	12
4	-49	-22
5	83	-78
6	-39	6

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[a] Within each group are the values of k, $10F_o$, and $10F_c$. A negative sign preceding $10F_o$ should read "less than."

position of the hydrogen attached to the oxygen atom was determined in this way, while the positions of the others, which were coplanar with the organic unit, were assumed. The final cycles of full-matrix least-squares refinement were carried out using the weights which were calculated for each reflection on the basis of the reliability of the original film readings. The final R value was 0.083. Table I gives a listing of calculated and observed structure factors. Tables II and III give the final atomic coordinates and the anisotropic thermal parameters. Table IV gives the bond distances and bond angles.

Table II

Atomic Coordinates[a]

Atom	X	Y	Z
Se	0.2604 (1)	0.1592 (1)	0.3239 (2)
O	0.1657 (7)	0.0965 (5)	0.1805 (12)
Cl(1)	0.3869 (3)	0.1792 (2)	0.1553 (5)
Cl(2)	0.1454 (2)	0.1699 (2)	0.6288 (5)
Cl(3)	0.3753 (3)	0.0580 (2)	0.5213 (5)
N	0.9179 (9)	0.2196 (6)	0.3238 (14)
O	0.9111 (8)	0.0368 (5)	0.3256 (14)
C(1)	0.6295 (13)	0.0934 (10)	−0.0025 (23)
C(2)	0.6338 (10)	0.1866 (9)	−0.0039 (21)
C(3)	0.7221 (12)	0.0380 (8)	0.1027 (18)
C(4)	0.7315 (10)	0.2316 (8)	0.1044 (18)
C(5)	0.7435 (11)	0.3282 (8)	0.1096 (20)
C(6)	0.8181 (11)	0.0828 (8)	0.2113 (18)
C(7)	0.8233 (9)	0.1759 (7)	0.2094 (17)
C(8)	0.8411 (12)	0.3701 (8)	0.2249 (21)
C(9)	0.9320 (13)	0.3143 (8)	0.3323 (23)
H(1)	0.72	−0.04	0.10
H(2)	0.55	0.06	−0.07
H(3)	0.56	0.22	−0.09
H(4)	0.68	0.37	0.03
H(5)	0.85	0.45	0.23
H(6)	0.01	0.35	0.42
H(7)	0.98	0.18	0.41
H(8)	0.89	−0.03	0.29

[a] Estimated standard deviations × 10^4 are given in parentheses.

Table III

Anisotropic Thermal Parameters[a]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Se	85 (1)	42 (1)	306 (4)	−1 (1)	77 (3)	−4 (2)
O	104 (8)	48 (4)	324 (22)	−32 (8)	27 (20)	−31 (14)
Cl(1)	98 (3)	62 (2)	352 (10)	−20 (3)	123 (8)	−28 (5)
Cl(2)	86 (2)	39 (1)	315 (8)	−6 (2)	84 (6)	−6 (4)
Cl(3)	111 (3)	55 (2)	380 (10)	54 (3)	79 (8)	59 (6)
N	93 (8)	48 (5)	285 (25)	15 (10)	124 (22)	35 (16)
O	111 (8)	32 (3)	390 (24)	15 (8)	29 (22)	19 (13)
C(1)	121 (13)	75 (8)	391 (41)	−72 (15)	−1 (36)	−20 (27)
C(2)	76 (9)	82 (3)	326 (36)	49 (12)	107 (27)	41 (24)
C(3)	115 (12)	52 (5)	269 (32)	−37 (13)	71 (29)	5 (19)
C(4)	86 (9)	52 (5)	318 (31)	30 (11)	131 (27)	45 (20)
C(5)	96 (10)	54 (6)	322 (36)	33 (12)	110 (30)	1 (21)
C(6)	106 (11)	50 (5)	257 (28)	4 (12)	156 (28)	7 (18)
C(7)	83 (9)	40 (5)	264 (27)	0 (10)	70 (24)	−28 (16)
C(8)	131 (13)	47 (5)	407 (39)	58 (12)	176 (36)	81 (21)
C(9)	132 (14)	51 (6)	355 (39)	17 (14)	176 (36)	15 (22)

[a] Estimated standard deviations × 10^4 are given in parentheses. The temperature factor is in the form: $T_i = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)_i]$.

Discussion

The structure can best be described as consisting of chains of selenium oxyhalide units oriented parallel to the c axis, with the organic cations packed around the chains. Figure 1 shows an end view of this chain structure, as viewed down the c axis. Figure 2 shows the bc projection, which is parallel with the chain units. The bridging chlorine, Cl(2), is hydrogen bonded to both the nitrogen and the oxygen of the organic cation. Bond distances and angles for the organic cation are shown in Figure 3, and the bond angles around the selenium are shown in Figure 4. The temperature factors appear reasonable: the organic ring appears to

Table IV

Bond Distances and Angles in and Around the Anion Chain[a]

	Distance, A		Angle, deg
Se–O	1.594 (9)	O–Se–Cl(1)	102.3 (0.3)
Se–Cl(1)	2.271 (4)	O–Se–Cl(2)	95.2 (0.3)
Se–Cl(2)	2.963 (3)	O–Se–Cl(3)	104.0 (0.3)
Se–Cl(3)	2.234 (4)	O–Se–Cl′(2)	90.8 (0.3)
Se–Cl′(1)	3.380 (4)	O–Se–Cl′(1)	161.6 (0.3)
Se–Cl′(2)	2.992 (3)	Cl(1)–Se–Cl(3)	91.1 (0.1)
Se–Se′	4.471 (2)	Cl(3)–Se–Cl(2)	85.1 (0.1)
O–Cl(1)	3.041 (9)	Cl(2)–Se–Cl′(2)	92.3 (0.1)
O–Cl(2)	3.490 (9)	Cl′(2)–Se–Cl(1)	87.0 (0.1)
O–Cl(3)	3.041 (10)	Cl′(1)–Se–Cl(1)	92.6 (0.1)
O–Cl′(2)	3.410 (8)	Cl′(1)–Se–Cl(3)	86.2 (0.1)
Cl(1)–Cl(3)	3.215 (5)	Cl′(1)–Se–Cl(2)	70.1 (0.1)
Cl(2)–Cl(3)	3.556 (4)	Cl′(1)–Se–Cl(2)	79.2 (0.1)
Cl(1)–Cl′(1)	4.156 (5)	Cl(3)–Se–Cl′(2)	165.1 (0.1)
Cl(1)–Cl′(2)	3.660 (4)	Cl(2)–Se–Cl(1)	162.5 (0.1)
Cl(3)–Cl′(3)	3.606 (5)	Se–Cl(1)–Se′	102.8 (0.1)
Cl(2)–O(org)	3.119 (8)	Se–Cl(2)–Se′	97.3 (0.1)
Cl(2)–N	3.091 (12)		

[a] Primed symbols represent atoms in an adjacent asymmetric unit (see Figure 1). Standard deviations (distances × 10^3 A, angles in degrees) are given in parentheses.

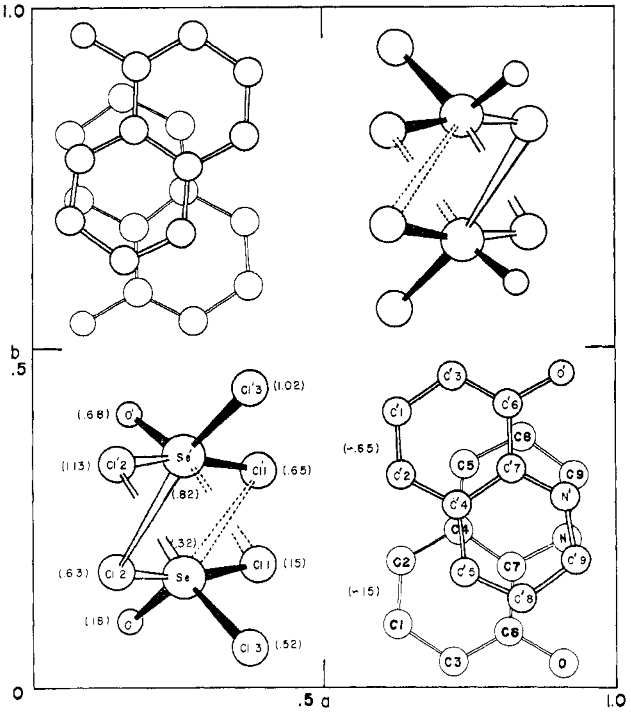

Figure 1.—View down the c axis. The c coordinates (elevations) are given in parentheses for the heavy atoms and for the approximate level of the planar organic cations which are nearly parallel to the plane of this projection. The solid, dark lines indicate the Se–O bonds and the short (2.2- and 2.3-A) Se–Cl bonds. The undarkened lines indicate the bridging (3.0-A) Se–Cl–Se bonds, and the single dotted lines show the nearest approach of a chlorine to the sixth position of the distorted octahedra around the selenium. The dotted lines show the N–H···Cl and O–H···Cl bonds.

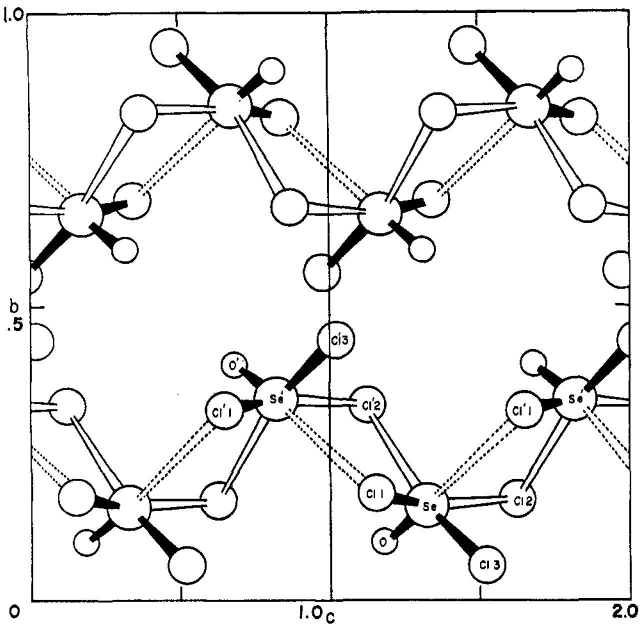

Figure 2.—View down the *a* axis.

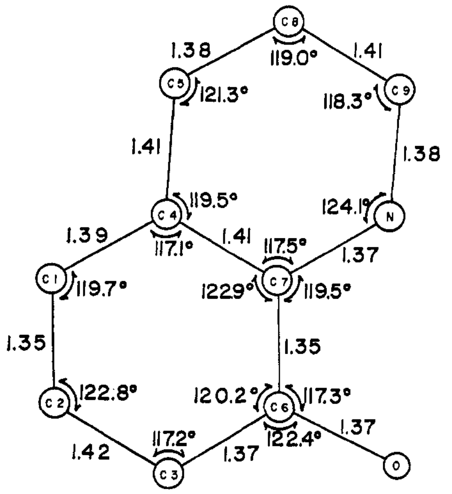

Figure 3.—Bond distances and angles for the 8-hydroxyquinolinium ion. The standard deviation of each given distance is 0.02 A, and the average standard deviation of the given angles is 1.0°.

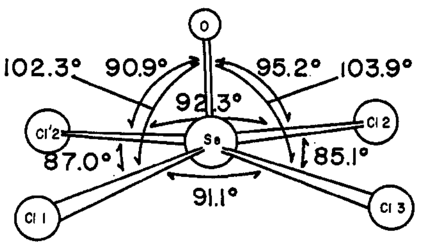

Figure 4.—Bonding angles around the selenium. In this figure, the oxygen is above the selenium. The two chlorine atoms in the foreground have the shorter (2.3-A) Se–Cl bonds, while those in the back are the bridging units at 3.0 A.

vibrate as a rigid body, and the one chlorine with less thermal motion than the others is the bridging atom.

The environment of each selenium atom is of considerable interest. Each selenium is surrounded by one oxygen and five chlorine atoms. The selenium–oxygen bond distance (1.59 A) is equal to that found in the 1:2 addition compound of selenium oxychloride and pyridine[3] and is comparable to the selenium–oxygen distance found in an electron diffraction study of $SeOCl_2$ (1.61 A). The five selenium–chlorine distances vary considerably; two of these, 2.23 and 2.27 A, are similar to values found by McCullough for a number of selenium–chlorine compounds.[7,8] Two other chlorine atoms, at 2.96 and 2.99 A, are almost exactly equidistant between two selenium atoms. The fifth chlorine neighbor of each selenium is at a distance of 3.3 A. This value is thus shortened only a small amount from the sums of the nonbonding radii, 3.8 A.

Discussion of the bonding of the selenium atom is certainly dependent on the bonding interpretation of the 2.96- and 2.99-A selenium–chlorine bonds. If these distances are considered too long to be covalent bonds and interpreted as some type of ion–dipole association, the compound is best described by the formula RH^+-Cl^-·$SeOCl_2$. The very short hydrogen bonds of the chloride bridge suggest an ionic nature for Cl(2). Selenium oxydichloride has received considerable attention as a solvent, and its ability to accept chloride ions has been described as part of the reaction of a base (chloride ion donor) with this solvent. Compounds of the formula $MCl·SeOCl_2$ have been isolated for potassium, rubidium, and cesium chlorides.[9] Pyridinium chloride, quinolinium chloride, and isoquinolinium chloride dissolve in selenium oxydichloride, and compounds of stoichiometry $RHCl·(SeOCl_2)_2$ can be isolated.[10] Tetramethylammonium chloride dissolved in selenium oxydichloride has yielded solids of the composition $(CH_3)_4NCl·5SeOCl_2$, $(CH_3)_4NCl·3SeOCl_2$, and $(CH_3)_4NCl·2SeOCl_2$.[11] From this it appears that the present structure is perhaps only one example of a number of possible selenium oxychloride–chloride bridging systems.

It is also interesting to take the approach that the selenium and chlorine atoms separated by 2.96 and 2.99 A are close enough to represent a definite interaction of filled orbitals from the chloride ion with vacant d orbitals on the selenium. This more covalent approach can be supported by the fact that these distances are almost 1 A shorter than the sum of the van der Waals bonds (3.8 A) and they form ClSeX angles very near 90° with the rest of the selenium unit. In this way the valency shell of Se would contain bonding electrons for one oxygen and four (unequal) chlorine bonds, plus a lone pair of electrons. Such an arrangement would be expected to yield a disordered octahedral arrangement of electron zones about the selenium and a disordered square-pyramidal arrangement of atoms.[12]

A complete rationalization of a structure such as this one is extremely difficult, if not impossible, until

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[7] J. D. McCullough and G. Hamburger, *J. Am. Chem. Soc.*, **64**, 508 (1942).

[8] J. D. McCullough and R. E. Marsh, *Acta Cryst.*, **3**, 41 (1950).

[9] C. R. Wise, *J. Am. Chem. Soc.*, **45**, 1233 (1923).

[10] J. Jackson and G. B. L. Smith, *ibid.*, **62**, 544 (1940).

[11] M. Agerman, L. H. Anderson, I. Lindquist, and M. Zackrisson, *Acta Chem. Scand.*, **12**, 477 (1958).

[12] R. S. Gillespie, *J. Am. Chem. Soc.*, **82**, 5978 (1960).

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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(1) Department of Chemistry, University of Canterbury, Christchurch, New Zealand.

(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).