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The Crystal and Molecular Structure of the Five-Coordinate Complex Dichloro-1,1,7,7-tetraethyldiethylenetriaminecobalt(II)

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The crystal and molecular structure of Co(Et$_4$dien)Cl$_2$, in which Et$_4$dien is the bulky ligand 1,1,7,7-tetraethyldiethylenetriamine, has been determined from three-dimensional X-ray data collected from a single crystal. The material crystallizes in the space group P$\bar{1}$ of the triclinic system, with two molecules in a cell of dimensions $a = 7.04$ A, $b = 12.99$ A, $c = 9.90$ A, $\alpha = 68.1°$, $\beta = 80.9°$, and $\gamma = 79.7°$. The coordination geometry of Co(Et$_4$dien)Cl$_2$ is distorted and cannot be viewed simply as either a square pyramid or a trigonal bipyramid. Various features of the molecular geometry of Co(Et$_4$dien)Cl$_2$ are compared with the structural results reported for other related complexes. The stability order found in polar organic solvents for the five-coordinate complexes Ni(Et$_4$dien)X$_2$ (X = Cl, Br, I) is interpreted in terms of the observed steric crowding in the molecular structure of the five-coordinate Co(Et$_4$dien)Cl$_2$ complex.

Introduction

Recent studies have produced examples of high-spin, five-coordinate complexes of the first-row transition metal ions.[2-8] These complexes invariably contain σ-bonding light-donor-atom ligands which are sufficiently bulky so that the tendency to attain six-coordination with central metals such as Ni(II) and Co(II) is suppressed.

Two ligands which have played an important role in these studies are 1,1,4,7,7-pentamethyldiethylenetriamine (Me$_5$dien) and 1,1,7,7-tetraethyldiethylenetriamine (Et$_4$dien). Of particular interest is the fact that, whereas both ligands form high-spin, five-coordinate complexes of the type CoLX$_2$ (X = Cl, Br), only Me$_5$dien forms high-spin NiLX$_2$ complexes which are five-coordinate in the solid state; the Ni(Et$_4$dien)X$_2$ complexes are low-spin and four-coordinate in the solid and in ethanol solution. It is reasonable to assume that electronic factors do not change in going from Me$_5$dien to Et$_4$dien and, therefore, that the observed change in coordination number for Ni(II) is mainly due to steric factors. Thus, replacement of the methyl groups by the more bulky ethyl groups presumably tips the balance in favor of a four-coordinate form for Ni(Et$_4$dien)X$_2$.

Prior to the structural studies described above, the ligand Et$_4$dien had been employed in studies of steric factors in square-planar substitution processes for the substrate Pd(Et$_4$dien)Cl$^+$.[9] More recently, these mechanistic studies have been extended to include the substrates Pt(Et$_4$dien)Cl$^+$ [10a] and Au(Et$_4$dien)Cl^{2+}.[10b] Since the proposed pathway for square-planar substitution reactions includes a five-coordinate intermediate,[11] it is clear that the structure of a ground-state five-coordinate complex containing Et$_4$dien would be of considerable interest. In addition, the striking structural contrast displayed in the Ni(II) systems with Me$_5$dien and Et$_4$dien makes it desirable to have detailed structural results available in analogous complexes containing these ligands.

We have investigated the structure of Co(Et$_4$dien)-Cl$_2$ by single-crystal X-ray diffraction methods. A discussion of the structural and stability patterns of complexes containing Me$_5$dien, Et$_4$dien, and related ligands is presented in this paper.

Collection and Reduction of the X-Ray Data

The red-purple crystals of Co(Et$_4$dien)Cl$_2$ were examined by optical, precession, and Weissenberg techniques and were found to belong to the triclinic system. A Delauny reduction failed to suggest the presence of hidden symmetry. A convenient cell chosen for the indexing of the Weissenberg photographs has the dimensions $a = 7.041 \pm 0.02$ A, $b = 12.99 \pm 0.03$ A, $c = 9.90 \pm 0.02$ A, $\alpha = 68.1 \pm 0.3°$, $\beta = 80.9 \pm 0.3°$, $\gamma = 79.7 \pm 0.3°$, and cell volume = 826 A^3. An experimental density of 1.41 g/cm^3 obtained by flotation in CCl$_4$–benzene solution agrees well with the density of 1.39 g/cm^3 calculated for two molecules in the primitive cell. A negative piezoelectric test indicated the centrosymmetric space group P$\bar{1}$.[12] The satisfactory agreement ultimately obtained between observed and calculated structure factors confirms this choice.

Intensity data were collected at room temperature by the integrating equiinclination Weissenberg technique. Zirconium-filtered Mo Kα radiation was employed. The layers 0*kl* to 6*kl* were photographed and the intensities of 1051 independent reflections accessible

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(12) We thank Dr. James A. Ibers for this experimental investigation.

within the angular range $\theta_{\mathrm{Mo}} \leqslant 22.0°$ were estimated visually. Because of the triclinic symmetry, the intensity estimates were made from both the top and bottom portions of the films, and no correction was applied for spot elongation. The usual Lorentz-polarization factors were applied to the intensities to yield F_o^2 (where F_o is the observed structure amplitude). Because of the smallness of the absorption coefficient (μ = 13.8 cm^{-1}) and the uniformity of the crystal dimensions, no absorption correction was applied. The F_o values were subsequently brought to an approximate scale through a modification of Wilson's procedure.

Solution of the Structure

The positions of the cobalt and the two chlorine atoms were readily determined from a three-dimensional Patterson function.[13] These positional parameters, along with variable isotropic temperature factors assigned to each of the atoms, were refined through several cycles of least squares. All nitrogen and carbon atoms were then located on subsequent difference Fouriers based on phases obtained from the heavy atoms.

The complete trial structure was refined by a least-squares procedure. The function minimized was $\Sigma w(F_o - F_c)^2$, where the weights were assigned in the following ways: $I \leqslant 5, w = (I/5)^2$; $5 < I < 175, w = 1$; $I \geqslant 175, w = (175/I)^2$; I is the average raw intensity for the particular reflection. The atomic scattering factors for the neutral atoms tabulated by Ibers[14] were used. The anomalous parts of the Co and Cl scattering factors were obtained from Templeton's tabulation[15] and were included in the calculated structure factors.[16]

An initial refinement was carried out in which all atoms were assigned individual isotropic thermal parameters. This refinement of 79 positional scale and thermal parameters converged to a conventional R factor ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.16 and to a weighted R factor R' ($R' = (\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2}$) of 0.17. After correction of several indexing errors the agreement factors dropped to R = 0.13 and R' = 0.13 for 1036 independent nonzero reflections. A different Fourier revealed anisotropic motion of the heavy atoms.

In a second round of calculations the Co and Cl atoms were allowed to vibrate anisotropically, while the other atoms were restricted to isotropic vibration. The scale factors and anisotropic thermal parameters were not refined simultaneously in the least squares. The final refinement of 87 positional and thermal parameters converged to an R factor of 0.117 and a weighted R factor R' of 0.117. The highest peak on the difference Fourier based on this refinement is 0.82 e/A^3, about 25% the height of a carbon atom. In Table I we list the final parameters obtained from the calculations in which Co and Cl were allowed to vibrate anisotropically. The final values of observed and calculated structure amplitudes are listed in Table II.

Table I

Positional and Thermal Parameters for Co(Et$_4$dien)Cl$_2$

Atom	x	y	z	$\beta_{11}{}^a$ or B, A^2
Co	0.0230 (4)[b]	0.2119 (3)	0.2137 (3)	0.0093 (6)
Cl$_1$	−0.2261 (6)	0.3475 (4)	0.1075 (5)	0.0207 (2)
Cl$_2$	−0.1278 (8)	0.0481 (4)	0.3003 (5)	0.0151 (2)
N$_1$	0.084 (2)	0.305 (1)	0.345 (1)	1.7 (3)
N$_2$	0.263 (2)	0.099 (1)	0.323 (1)	2.7 (3)
N$_3$	0.220 (2)	0.204 (1)	0.022 (1)	0.9 (2)
C$_1$	0.251 (5)	0.481 (2)	0.301 (3)	6.4 (7)
C$_2$	0.178 (3)	0.401 (2)	0.233 (2)	2.8 (4)
C$_3$	0.092 (4)	−0.344 (2)	−0.420 (2)	4.1 (5)
C$_4$	0.227 (4)	−0.251 (2)	−0.499 (3)	4.8 (4)
C$_5$	0.046 (4)	−0.187 (2)	0.116 (2)	3.8 (5)
C$_6$	0.154 (3)	0.135 (2)	−0.0521 (1)	2.9 (4)
C$_7$	0.232 (1)	0.324 (2)	−0.087 (2)	2.6 (4)
C$_8$	0.377 (2)	0.326 (1)	−0.227 (2)	3.8 (5)
C$_9$	0.407 (1)	0.143 (1)	0.073 (2)	2.6 (4)
C$_{10}$	0.390 (1)	0.052 (1)	0.219 (2)	2.9 (4)
C$_{11}$	0.379 (2)	0.157 (1)	0.389 (2)	2.3 (4)
C$_{12}$	0.216 (2)	0.227 (2)	0.454 (2)	3.3 (5)

Atom	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.0033 (2)	0.0047 (3)	−0.0028 (3)	0.0004 (1)	−0.0014 (2)
Cl$_1$	0.0042 (4)	0.0079 (8)	0.0001 (2)	−0.0033 (6)	−0.0013 (5)
Cl$_2$	0.0047 (4)	0.0081 (7)	−0.0054 (7)	0.0004 (3)	−0.0010 (4)

[a] The form of the anisotropic thermal 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.

The final R value of 0.117 is somewhat higher than we would normally expect, and we attribute this mainly to intensity errors arising from spot elongation and contraction.

Discussion

The structure described by the space group, the atomic parameters, and the unit cell constants consists of the packing of discrete molecules of Co(Et$_4$dien)Cl$_2$. The closest Co–Co approach is 8.04 A and all intermolecular contacts appear normal. Figure 1 is a perspective drawing of an isolated molecule of the complex.

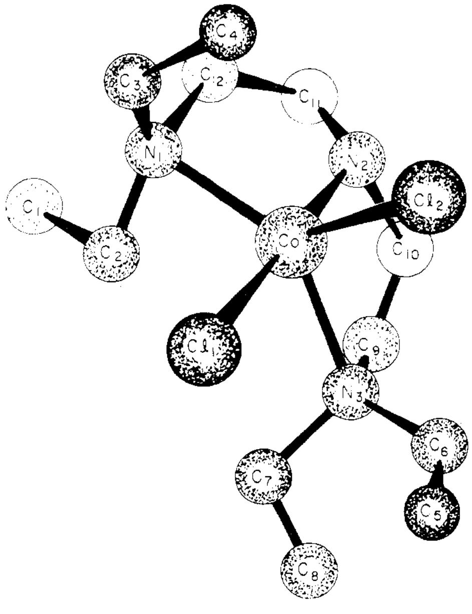

Figure 1.—Perspective drawing of the molecular structure of Co(Et$_4$dien)Cl$_2$.

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[13] Programs for the IBM 7094 used in this work were local modifications of Zalkin's FORDAP Fourier program, the Busing–Levy ORFLS least-squares program, and various crystallographic programs written at Brookhaven National Laboratory.

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

[15] D. H. Templeton, ref 14, Table 3.3.2C.

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

TABLE II

CALCULATED AND OBSERVED STRUCTURE AMPLITUDES FOR $Co(Et_4dien)Cl_2$

K	L	OBS	CAL
******H= 0******			
0	0	3092	0
5	0	329	266
6	0	230	220
7	0	587	576
8	0	271	231
9	0	251	227
11	0	285	239
12	0	181	176
3	1	268	273
4	1	338	287
5	1	167	136
6	1	331	309
7	1	309	293
8	1	198	188
9	1	151	187
10	1	111	123
11	1	84	116
-2	1	69	77
-3	1	80	64
-4	1	274	246
-5	1	433	433
-6	1	710	722
-8	1	232	229
-11	1	88	116
3	2	117	108
5	2	75	81
6	2	58	106
7	2	380	437
8	2	525	480
10	2	149	200
11	2	117	165
-1	2	301	273
-2	2	387	413
-3	2	212	184
-4	2	455	440
-5	2	295	268
-6	2	363	334
-7	2	195	177
1	3	359	329
2	3	1009	964
4	3	398	382
5	3	110	154
6	3	305	340
7	3	277	257
9	3	425	436
11	3	183	232
12	3	87	135
-1	3	128	134
-5	3	694	653
-6	3	208	229
-7	3	108	162
0	4	185	168
1	4	456	388
3	4	640	704
7	4	311	305
5	4	384	336
6	4	108	129
8	4	258	255
12	4	345	249
-3	4	65	103
-4	4	708	665
-5	4	241	242
-6	4	334	338
2	5	497	491
3	5	280	257
4	5	507	534
5	5	244	238
6	5	385	432
7	5	69	78
9	5	252	221
10	5	253	265
11	5	84	154
13	5	160	196
-1	5	65	124
-2	5	152	200
-3	5	415	455
-5	5	381	391
-6	5	82	126
0	6	70	144
2	6	95	108
5	6	173	168
6	6	343	387
9	6	214	202
11	6	148	196
13	6	94	137
-1	6	228	290
-2	6	236	257
-3	6	245	324
-4	6	203	233
0	7	272	265
2	7	165	169
3	7	199	220
5	7	352	372
10	7	147	191
12	7	92	141
-2	7	460	415
4	8	246	203
6	8	204	232
8	8	145	187
10	8	89	118
-1	8	385	352
-3	8	90	143
0	9	277	274
5	9	217	216
6	9	150	149
7	9	237	239
8	9	154	149
9	9	324	280
10	9	161	168
-1	9	91	118
7	10	131	229
******H= 1******			
4	0	592	691
5	0	491	433
6	0	210	168
7	0	299	336
8	0	175	172
9	0	355	385
11	0	313	314
-3	0	132	144
-4	0	49	58
-5	0	378	373
-6	0	219	232
-7	0	522	456
-8	0	157	169
-10	0	139	209
-12	0	280	309
4	1	44	15
5	1	325	260
6	1	308	247
7	1	332	305
9	1	282	254
10	1	415	393
11	1	245	236
-2	1	40	28
-4	1	158	187
-5	1	375	414
-6	1	474	517
-8	1	145	164
-9	1	78	101
-11	1	151	207
4	2	139	158
5	2	642	679
6	2	147	105
7	2	187	200
8	2	292	293
10	2	282	253
12	2	335	329
-1	2	547	517
-2	2	339	306
-3	2	220	179
-4	2	750	677
-5	2	351	403
-6	2	434	388
-7	2	123	146
0	3	102	137
2	3	670	754
3	3	600	589
4	3	640	608
5	3	190	118
6	3	583	593
7	3	184	200
8	3	65	84
9	3	180	160
11	3	79	146
13	3	197	257
-1	3	515	443
-3	3	572	582
-5	3	459	493
-6	3	232	189
0	4	350	365
1	4	338	373
2	4	186	183
3	4	453	441
4	4	259	218
5	4	447	463
6	4	266	227
7	4	360	395
8	4	133	134
10	4	75	19
-1	4	56	109
-2	4	340	353
-3	4	222	173
-4	4	374	377
-5	4	233	216
1	5	473	442
2	5	358	309
3	5	129	128
4	5	131	163
6	5	627	569
7	5	205	227
8	5	242	213
9	5	289	294
10	5	132	174
12	5	119	142
13	5	125	179
-1	5	307	319
-2	5	290	260
-3	5	253	267
-6	5	321	329
0	6	236	230
1	6	303	274
3	6	200	220
4	6	360	360
5	6	131	159
6	6	296	265
7	6	306	274
8	6	580	557
9	6	194	221
11	6	227	255
13	6	223	228
-1	6	228	259
-3	6	367	360
-4	6	136	176
-5	6	164	173
0	7	269	282
1	7	236	210
2	7	338	357
3	7	175	216
5	7	222	246
7	7	352	370
9	7	413	413
10	7	141	188
-2	7	437	409
-4	7	85	131
0	8	114	84
2	8	77	56
3	8	280	312
9	8	221	168
10	8	299	221
11	8	176	119
-2	8	85	70
1	9	147	53
2	9	145	199
5	9	83	54
8	9	121	63
9	9	87	237
3	10	155	153
7	10	89	136
8	10	91	92
3	-1	1041	917
4	-1	112	91
5	-1	344	303
6	-1	199	257
7	-1	93	124
8	-1	232	272
10	-1	363	399
11	-1	85	145
-3	-1	554	560
-4	-1	118	72
-5	-1	53	136
-6	-1	568	533
-8	-1	424	382
-9	-1	127	125
-10	-1	78	115
1	-2	94	107
2	-2	119	106
4	-2	228	219
5	-2	85	173
6	-2	65	65
7	-2	99	90
8	-2	149	183
9	-2	300	273
11	-2	89	94
-2	-2	628	732
-3	-2	262	225
-4	-2	272	218
-6	-2	101	141
-7	-2	493	467
-8	-2	314	275
-9	-2	162	177
-10	-2	77	75
0	-3	333	311
1	-3	283	298
3	-3	319	306
4	-3	478	436
5	-3	66	99
6	-3	156	159
7	-3	166	216
9	-3	118	178
10	-3	88	162
-1	-3	985	1025
-2	-3	689	677
-3	-3	49	97
-4	-3	219	242
-5	-3	449	379
-7	-3	351	312
-8	-3	374	308
-9	-3	405	373
1	-4	462	449
3	-4	127	126
4	-4	539	440
5	-4	274	291
6	-4	289	303
8	-4	407	370
-1	-4	436	513
-2	-4	244	218
-3	-4	710	687
-4	-4	395	341
-5	-4	103	121
-6	-4	250	231
-8	-4	390	377
-10	-4	435	378
0	-5	161	143
1	-5	166	200
2	-5	267	287
3	-5	389	381
5	-5	345	325
6	-5	114	151
7	-5	347	297
-2	-5	338	401
-3	-5	190	179
-4	-5	406	429
-5	-5	377	426
-7	-5	138	163
-8	-5	125	164
-9	-5	423	376
-10	-5	138	179
-11	-5	118	164
0	-6	252	244
1	-6	346	306
4	-6	259	290
6	-6	172	164
-3	-6	465	533
-4	-6	270	304
-5	-6	69	112
-10	-6	219	261
-11	-6	229	233
2	-7	178	223
3	-7	257	300
5	-7	88	113
-3	-7	222	185
-4	-7	292	302
-5	-7	243	284
-7	-7	173	173
-10	-7	258	240
1	-8	317	295
3	-8	89	161
-3	-8	79	138
-4	-8	259	286
-6	-8	264	322
-9	-8	86	112
0	-9	237	273
-5	-9	476	430
-6	-9	192	216
-7	-9	195	180
-8	-9	198	177
******H= 2******			
4	0	715	696
5	0	397	389
7	0	147	167
9	0	200	242
10	0	82	140
11	0	235	285
12	0	159	185
-2	0	334	363
-3	0	705	681
-5	0	333	307
-4	0	146	161
-7	0	223	226
-8	0	240	230
-10	0	218	209
4	1	523	492
5	1	230	220
6	1	593	563
8	1	97	142
10	1	395	401
11	1	229	265
13	1	164	172
-2	1	651	687
-3	1	490	520
-4	1	98	105
-5	1	139	170
-6	1	117	44
-10	1	126	14
4	2	601	558
5	2	1013	1040
7	2	404	421
8	2	183	168
9	2	197	177
10	2	211	183
12	2	338	348
-1	2	218	266
-2	2	821	931
-3	2	333	309
-4	2	280	230
-6	2	71	79
-7	2	353	339
-8	2	141	180
-9	2	123	151
3	3	169	144
4	3	736	700
6	3	959	908
7	3	460	384
12	3	236	242
-1	3	633	705
-2	3	340	365
-3	3	368	387
-5	3	235	276
-6	3	251	250
-8	3	317	320
0	4	461	463
1	4	350	335
5	4	444	380
6	4	225	286
7	4	215	246
8	4	327	308
12	4	87	136
13	4	130	208
-2	4	109	129
-4	4	72	89
-6	4	81	97
-7	4	231	276
0	5	523	498
1	5	284	249
2	5	495	453
5	5	231	179
6	5	205	199
7	5	331	357
8	5	143	142
9	5	232	234
11	5	167	166
12	5	88	110
-1	5	246	235
-6	5	272	264
0	6	192	209
1	6	619	615
3	6	279	269
8	6	501	466
10	6	259	251
12	6	155	170
13	6	210	216
-1	6	262	283
-3	6	80	100
-4	6	187	200
-6	6	205	201
0	7	246	224
2	7	498	466
3	7	193	199
4	7	192	178
8	7	112	61
10	7	147	108
12	7	130	82
-3	7	217	170
-5	7	289	274
1	8	295	251
2	8	141	160
3	8	370	344
4	8	240	245
8	8	279	267
9	8	172	234
10	8	178	194
11	8	92	121
2	9	176	161
3	9	352	303
4	9	86	149
5	9	86	143
10	9	252	272
4	10	243	280
6	10	141	171
8	10	134	130
2	-1	267	313
3	-1	864	930
4	-1	53	42
5	-1	263	287
7	-1	120	92
10	-1	391	452
11	-1	127	183
-2	-1	526	477
-4	-1	551	506
-5	-1	82	36
-7	-1	98	11
-8	-1	229	162
-9	-1	200	242
-10	-1	147	152
-12	-1	212	65
0	-2	438	376
1	-2	65	86
2	-2	912	771
3	-2	171	144
4	-2	592	620
5	-2	128	147
6	-2	69	81
8	-2	79	108
9	-2	348	414
11	-2	162	206
-2	-2	493	495
-3	-2	366	378
-4	-2	147	207
-5	-2	288	274
-7	-2	403	408
-8	-2	128	129
-9	-2	79	130
-10	-2	168	161
-12	-2	183	193
0	-3	511	437
1	-3	400	377
2	-3	422	394
3	-3	718	758
4	-3	241	265
6	-3	274	233
8	-3	308	281
9	-3	88	122
10	-3	309	241
-1	-3	380	376
-2	-3	236	237
-4	-3	100	72
-5	-3	307	313
-6	-3	147	111
-7	-3	259	197
-8	-3	248	313
-11	-3	89	93
1	-4	559	578
2	-4	315	323
3	-4	178	212
4	-4	298	300
6	-4	159	166
8	-4	240	277
9	-4	161	220
-1	-4	149	189
-4	-4	513	476
-5	-4	65	70
-6	-4	476	442
-7	-4	145	165
-8	-4	318	328
-11	-4	155	198
0	-5	468	429
2	-5	331	274
8	-5	163	89
-1	-5	66	62
-2	-5	236	236
-4	-5	68	122
-5	-5	322	373
-7	-5	348	376
-9	-5	294	258
0	-6	105	133
1	-6	171	183
2	-6	79	142
3	-6	141	163
6	-6	275	259
-1	-6	365	367
-3	-6	475	440
-4	-6	165	159
-5	-6	106	147
-6	-6	194	204
-7	-6	79	91
-8	-6	116	128
-10	-6	178	144
-11	-6	186	157
0	-7	213	235
3	-7	176	169
5	-7	163	167
-2	-7	238	203
-4	-7	201	240
-5	-7	161	160
-10	-7	185	151
0	-8	197	203
-3	-8	86	142
-4	-8	121	130
-6	-8	175	155
-7	-8	178	168
-9	-8	162	179
-3	-9	184	204
-5	-9	131	169
******H= 3******			
3	0	146	191
4	0	265	228
5	0	443	441
7	0	112	151
9	0	151	175
10	0	140	177
-2	0	375	437
-3	0	437	476
-4	0	95	154
-8	0	109	110
-9	0	143	172
-10	0	175	185
4	1	515	478
6	1	419	429
8	1	360	360
9	1	145	140
10	1	174	193
11	1	144	155
-1	1	321	372
-2	1	475	474
-3	1	89	130
-7	1	129	36
-9	1	85	60
4	2	250	200
5	2	539	489
6	2	55	105
7	2	625	593
8	2	66	125
9	2	596	580
12	2	173	192
-1	2	164	144
-2	2	539	583
-3	2	244	282
-7	2	325	323
-9	2	196	177
2	3	152	185
3	3	332	317
4	3	118	138
5	3	247	225
6	3	371	330
7	3	247	186
8	3	391	323
10	3	199	228
11	3	257	286
12	3	191	190
-1	3	461	482
-2	3	113	106
-4	3	168	178
-5	3	143	134
-6	3	437	458
-8	3	406	375
1	4	471	449
3	4	190	197
4	4	247	239
5	4	259	258
6	4	276	249
7	4	140	136
8	4	183	221
9	4	124	134
10	4	108	163
12	4	217	226
13	4	202	255
-1	4	83	63
-4	4	102	157
-6	4	291	292
-7	4	320	311
0	5	527	445
1	5	60	90
2	5	651	617
3	5	83	116
4	5	269	237
7	5	439	445
9	5	234	233
10	5	78	135
11	5	333	326
-1	5	93	136
-2	5	70	86
-5	5	260	248
-6	5	122	140
0	6	212	174
1	6	479	490
3	6	390	397
4	6	203	201
5	6	238	265
8	6	227	238
9	6	171	129
10	6	160	165
12	6	327	295
-1	6	103	14
-4	6	118	225
-5	6	87	22
2	7	273	308
4	7	331	253
5	7	102	23
7	7	280	295
8	7	134	129
9	7	80	101
-1	7	217	237
-3	7	122	143
-4	7	155	145
0	8	253	236
1	8	142	148
2	8	113	172
3	8	137	119
4	8	199	241
5	8	157	163
6	8	295	307
8	8	255	249
-2	8	235	180
3	9	266	263
5	9	170	170
7	9	260	283
10	9	129	136
6	10	158	156
3	-1	619	582
4	-1	311	303
5	-1	344	308
7	-1	213	184
8	-1	235	224
9	-1	111	132
10	-1	119	148
11	-1	154	179
-1	-1	84	143
-2	-1	577	624
-3	-1	346	414
-4	-1	502	549
-8	-1	131	7
-10	-1	86	8
1	-2	273	252
2	-2	533	533
4	-2	415	387
6	-2	286	281
8	-2	156	172
9	-2	297	337
-1	-2	209	252
-2	-2	240	295
-3	-2	575	628
-5	-2	349	301
-6	-2	173	179
-8	-2	151	182
-10	-2	412	335
0	-3	136	118
1	-3	275	268
2	-3	208	219
3	-3	577	582
4	-3	65	79
5	-3	216	216
6	-3	194	165
7	-3	243	262
8	-3	218	255
-1	-3	192	194
-4	-3	474	534
-5	-3	333	370
-6	-3	210	209
-7	-3	229	202
-9	-3	220	171
-11	-3	156	148
1	-4	483	413
2	-4	518	469
3	-4	314	296
5	-4	347	292
-4	-4	231	217
-5	-4	225	216
-6	-4	447	466
-11	-4	158	108
0	-5	313	310
1	-5	218	217
2	-5	191	177
3	-5	150	156
7	-5	244	247
-1	-5	96	173
-4	-5	139	145
-5	-5	338	317
-7	-5	204	172
1	-6	383	388
2	-6	333	310
6	-6	159	207
-2	-6	230	216
-4	-6	168	173
-6	-6	371	373
-8	-6	146	163
0	-7	480	428
2	-7	149	145
-2	-7	81	120
-5	-7	142	168
-6	-7	119	114
-7	-7	218	264
-8	-7	153	178
-9	-7	91	119
0	-8	178	204
-6	-8	89	135
-7	-8	230	231
******H= 4******			
3	0	101	109
4	0	92	107
5	0	214	103
7	0	416	362
8	0	257	222
9	0	402	423
10	0	210	211
-3	0	221	304
-5	0	207	226
-7	0	200	247
-9	0	229	225
4	1	184	180
5	1	166	135
6	1	110	92
7	1	137	143
8	1	433	462
10	1	217	229
11	1	83	106
-3	1	53	78
-4	1	266	277
-5	1	65	48
-6	1	226	215
-8	1	365	351
4	2	245	183
5	2	252	213
6	2	310	187
7	2	155	143
8	2	213	197
9	2	456	444
10	2	107	145
-3	2	316	378
-4	2	63	142
-5	2	271	229
-7	2	253	190
3	3	542	549
4	3	396	373
5	3	128	114
8	3	207	207
10	3	286	293
11	3	306	263
-1	3	171	232
-3	3	89	88
-4	3	337	319
-6	3	78	123
1	4	267	277
2	4	325	309
3	4	539	528
4	4	401	388
5	4	491	500
6	4	187	114
10	4	385	383
12	4	277	303
-2	4	208	199
-3	4	294	323
-4	4	146	157
-5	4	110	132
-6	4	143	187
0	5	176	148
2	5	298	263
3	5	188	173
4	5	513	524
5	5	160	148
6	5	289	288
7	5	207	186
11	5	348	382
12	5	86	159
-1	5	286	285
-2	5	99	114
-3	5	274	301
-5	5	186	216
0	6	100	54
1	6	136	174
3	6	65	78
4	6	65	88
5	6	334	289
6	6	219	177
10	6	213	224
12	6	243	264
-1	6	127	156
-2	6	251	245
-4	6	169	150
0	7	155	106
3	7	72	69
6	7	380	338
7	7	194	244
9	7	79	72
11	7	86	167
-1	7	179	188
-2	7	83	103
0	8	168	197
1	8	164	172
5	8	111	150
6	8	391	358
7	8	113	127
8	8	278	266
-1	8	87	122
2	9	174	183
3	9	148	150
5	9	220	219
7	9	292	356
1	-1	290	275
2	-1	182	212
3	-1	247	222
4	-1	289	262
6	-1	142	170
7	-1	425	411
8	-1	519	483
10	-1	84	143
-3	-1	265	290
-4	-1	293	299
-5	-1	89	172
-6	-1	118	154
-8	-1	157	48
0	-2	124	116
1	-2	407	439
2	-2	256	229
3	-2	180	122
4	-2	119	122
6	-2	416	359
8	-2	250	253
-1	-2	343	425
-3	-2	387	449
-6	-2	219	172
-7	-2	240	221
-8	-2	111	116
-10	-2	246	248
0	-3	416	321
1	-3	246	247
2	-3	219	205
3	-3	269	251
4	-3	66	108
5	-3	157	174
6	-3	129	144
7	-3	177	209
-1	-3	112	107
-2	-3	219	251
-4	-3	270	285
-5	-3	217	225
-7	-3	129	161
-9	-3	187	185
1	-4	212	186
2	-4	333	307
5	-4	200	204
6	-4	307	269
-1	-4	164	172
-2	-4	64	100
-3	-4	280	299
-5	-4	258	214
-6	-4	127	170
-7	-4	77	117
1	-5	201	266
5	-5	216	195
-1	-5	121	143
-3	-5	191	179
-4	-5	195	196
-5	-5	238	237
-6	-5	77	135
-7	-5	139	128
1	-6	158	175
3	-6	233	262
-2	-6	207	232
-4	-6	175	197
-6	-6	267	309
-8	-6	87	158
0	-7	189	178
2	-7	197	203
-3	-7	144	185
-5	-7	170	196
******H= 5******			
3	0	125	114
4	0	131	84
6	0	187	169
7	0	246	277
9	0	288	319
4	1	158	158
5	1	118	117
7	1	174	162
8	1	245	251
10	1	111	153
4	2	233	202
5	2	221	194
10	2	241	235
4	3	357	369
6	3	244	222
7	3	187	168
8	3	158	182
9	3	99	130
11	3	228	238
2	4	267	276
3	4	139	120
4	4	267	281
5	4	452	477
7	4	272	251
9	4	223	209
10	4	336	333
3	5	224	208
4	5	386	425
6	5	327	344
11	5	257	289
0	6	202	231
1	6	137	139
4	6	159	124
5	6	207	186
6	6	298	332
0	7	350	347
5	7	176	173
7	7	210	253
9	7	159	134
10	7	117	121
1	8	263	222
4	8	111	21
5	8	192	156
7	8	196	15
1	-1	347	355
2	-1	126	83
3	-1	154	114
6	-1	182	169
7	-1	272	307
8	-1	293	327
0	-2	125	101
1	-2	427	410
2	-2	152	138
3	-2	161	140
6	-2	305	278
7	-2	273	238
0	-3	489	430
1	-3	120	133
2	-3	152	148
3	-3	92	119
4	-3	137	177
5	-3	177	195
7	-3	255	248
1	-4	186	153
4	-4	151	148
5	-4	193	168
6	-4	301	372
0	-5	209	234
1	-5	106	147
3	-5	112	41
4	-5	260	250
******H= 6******			
5	1	288	357
6	1	140	139
7	1	219	231
8	1	246	260
9	1	229	208
5	2	164	181
6	2	250	282
7	2	260	227
3	3	75	13
6	3	104	81
7	3	213	225
8	3	245	251
9	3	113	115
6	4	167	125
7	4	266	276
8	4	75	54
9	4	299	279
9	5	209	229
8	5	219	273
5	6	149	159
6	6	152	138
8	6	142	141
4	7	209	201
5	7	142	152
7	7	170	196
0	-1	221	253
1	-1	208	250
3	-1	184	182
4	-1	126	99
5	-1	230	239
7	-1	81	127
0	-2	231	180
1	-2	232	218
2	-2	175	135
3	-2	210	155
5	-2	77	79
6	-2	142	166
0	-3	265	240
1	-3	240	172
4	-3	139	134
5	-3	120	123
1	-4	220	228
3	-4	191	176

In the molecule, cobalt is coordinated to the two chlorine and the three nitrogen atoms. The molecular geometry is quite irregular and could be viewed as either a distorted square pyramid or a distorted trigonal bipyramid. However, we find it more convenient in comparative structural discussions to utilize the "distorted square pyramid" description. The important intramolecular distances and angles are given in Table III. Co, N_1, N_2, and Cl_1 are coplanar. The equation of the best least-squares plane through these atoms is $4.438x + 4.232y - 5.075z = -8.291$ (triclinic coordinates). The deviations of the four atoms from this plane are presented in Table IV. The atom Cl_2 is very significantly displaced from the ideal apical position of a square pyramid based on the least-squares plane. This is logically the result of nonbonded repulsions between Cl_2, the terminal methyl group C_4, and Cl_1. The Cl_2–C_4 distance of 3.76 A is shorter than the sum of 3.8 A from the van der Waals radii of chlorine and a methyl carbon. Placing the atom Cl_2 in the ideal apical position would shorten the Cl_2–C_4 distance to about 3.2 A. The Cl_1–Cl_2 distance is 3.62 A and the Cl_1–Co–Cl_2 bond

TABLE III

SELECTED INTRAMOLECULAR DISTANCES AND ANGLES

Intramolecular distances, A		Angles, deg	
Co–Cl_1	2.319 (6)	Cl_1–Co–Cl_2	101.8 (3)
Co–Cl_2	2.357 (7)	N_1–Co–N_2	80.1 (3)
Co–N_1	2.21 (1)	N_1–Co–N_3	120.4 (4)
Co–N_2	2.16 (2)	N_2–Co–N_3	80.7 (2)
Co–N_3	2.19 (2)	Cl_1–Co–N_1	93.1 (3)
Cl_1–Cl_2	3.62 (2)	Cl_1–Co–N_2	173.4 (3)
N_1–N_2	2.81 (6)	Cl_1–Co–N_3	101.9 (3)
N_2–N_3	2.82 (5)	Cl_2–Co–N_1	126.8 (2)
Cl_1–C_2	3.56 (3)	Cl_2–Co–N_2	83.3 (3)
Cl_1–C_3	3.36 (3)	Cl_2–Co–N_3	105.9 (2)
Cl_1–C_6	4.07 (3)		
Cl_1–C_7	3.51 (3)		
Cl_2–C_4	3.76 (4)		
Cl_2–C_5	3.83 (3)		

TABLE IV

DEVIATION OF THE ATOMS OF Co, Cl_1, N_1, AND N_2 FROM THE LEAST-SQUARES PLANE

Atom	Distance, A
Co	−0.002 (2)
Cl_1	0.005 (4)
N_1	0.00 (2)
N_2	0.03 (2)

angle is 101.8°. The Cl_2 atom further distorts the coordination geometry by moving N_3 drastically from the basal plane of the pyramid. It should also be noted that the distances between Cl_1 and the four CH_2 groups —C_2, C_3, C_6, and C_7—are all shorter than the van der Waals radii sum of 3.8 A.[17] We view the extremely distorted geometry of the complex as a direct result of these strong nonbonded repulsions. Six-coordination in $Co(Et_4dien)Cl_2$ is effectively suppressed by these same steric factors; the methylene group, C_2, completely blocks the sixth coordination site of the cobalt.

The importance of steric crowding in determining the coordination geometry of these types of complexes is confirmed on comparing the structures of the complexes $Co(Me_5dien)Cl_2$ and $Co(Et_4dien)Cl_2$. There are significant differences in the coordination geometries in these two cases, including a considerably larger (135°) N_1–Co–N_3 angle in the $Co(Me_5dien)Cl_2$ complex.[4] Replacement of the ethyl groups by the smaller methyl groups should decrease the repulsions between the chlorine atoms and the terminal alkyl groups. As a result, we expect a smaller displacement of N_3 from the plane determined by the atoms Co, N_1, N_2, and Cl_1, as is observed.[4] Furthermore, the complex $Ni(Me_5dien)Cl_2$ is known to be five-coordinate in the solid state, whereas $Ni(Et_4dien)Cl_2$ is four-coordinate in that state. Assuming that the electronic factors do not change in going from Me$_5$dien to Et$_4$dien, we attribute this different behavior to a steric effect, namely, an increase in steric crowding in the inner coordination sphere in the case of Et$_4$dien. In addition, in polar organic solvents where both the four- and five-coordinate forms of the complexes $Ni(Et_4dien)X_2$ are observed, the fractional concentration of the five-coordinate form decreases considerably in the X series $Cl^- > Br^- > I^-$.[8] We have previously suggested steric crowding as the principal explanation for this stability order, and the observed structure of $Co(Et_4dien)Cl_2$ provides strong support. We are now investigating the structure of the square-planar complex $[Ni(Et_4dien)Br]Br$ by X-ray techniques and we await the result of this study to discuss the mechanism of substitution reactions in these types of complexes.

It is of interest to compare the structure of high-spin $Co(Et_4dien)Cl_2$ with that of the low-spin five-coordinate complex $Ni(triars)Br_2$.[18] In the case of the latter, the As donor atoms and the central metal lie effectively in the same plane, and the geometry can be described as a distorted square pyramid. It seems reasonable to suggest that electronic factors assume a larger structural role in the low-spin complex and that the presence of heavy-donor As atoms capable of good σ(ligand) $\rightarrow$ p(metal)[19] and possibly d_π(metal) $\rightarrow$ d_π-(ligand) bonding will favor an arrangement in which the metal and the heavy-donor As atoms are accommodated in the same plane. The steric strain in this five-coordinate structure is then reduced by perturbing the metal–halogen bonds. Therefore, the molecular geometry adopted by $Ni(triars)Br_2$ can be viewed as a compromise between electronic and steric factors of comparable importance. This is in contrast to the case of the $Co(Et_4dien)Cl_2$ complex, where the *principal* determinant of molecular geometry is apparently the quest for relief of steric strain.

Acknowledgment.—We thank the National Science Foundation for support of this research.

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[17] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, Table 7-20, p 260.

[18] G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc.*, 415 (1960).

[19] See the discussion in ref 11, pp 24–28.

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The Crystal Structure of Chloropentaamminecobalt(III) Hexafluorosilicate

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The crystal structure of chloropentaamminecobalt(III) hexafluorosilicate, $[Co(NH_3)_5Cl]SiF_6$, has been studied by optical and single-crystal X-ray methods. The complex crystallizes in the monoclinic system with $a = 6.26 \pm 0.01$, $b = 8.22 \pm 0.01$, $c = 10.18 \pm 0.02$ A; and $\beta = 99° 40' \pm 30'$. The space group is $P2_1/m$ with two formula weights in the unit cell. The structure has been determined and refined to an R factor of 0.12 for 649 reflections. The cation and anion exist as octahedra, and the measured Co–N distances show no evidence for a "*trans* effect" induced by the presence of the Cl atom. A preliminary examination of the corresponding cyano derivative, $[Co(NH_3)_5CN]SiF_6$, indicates that it is isomorphous with the chloro compound.

Introduction

While searching for salts of acidopentaammine cations, $[M(NH_3)_5X]^{2+}$, useful for single-crystal spectroscopy we have found those of the hexafluorosilicate anion to have many suitable features. No crystallographic studies have been reported on this family of salts other than an early observation[2] on the external crystal habit and that the crystals were noticeably dichroic.

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[1] (a) This paper is based in part on a thesis submitted by J. A. Stanko to the Graduate College of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry; (b) NSF Predoctoral Fellow, 1962–1965.

[2] S. M. Jorgensen, *J. Prakt. Chem.*, **18**, 230 (1878).