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Crystal and Molecular Structure of Dichlorobis(2-dimethylaminoethyl)methylaminecobalt(II)

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The crystal structure of $Co(Me_5dien)Cl_2$, in which Me_5dien is the ligand bis(2-dimethylaminoethyl)methylamine, has been determined from three-dimensional X-ray data collected by photographic methods. The crystals belong to the space group $P2_1/c$ with cell dimensions $a = 8.389 \pm 0.004$ Å, $b = 29.430 \pm 0.010$ Å, $c = 12.018 \pm 0.005$ Å, $\beta = 101°\,31' \pm 4'$. The density of 1.385 g cm^{-3} calculated for eight formula units in the cell is in agreement with the measured density of 1.38 g cm^{-3}. There are two crystallographically independent but essentially identical molecules in the cell. The structure has been refined by least-squares techniques to a final R factor of 8.2% for the 1567 independent observed reflections. The structure consists of discrete molecules in which cobalt(II) exhibits five-coordination, intermediate in shape between trigonal bipyramidal and square pyramidal and seemingly imposed essentially by the steric requirements of the ligands. A detailed study of the effects of steric repulsions on the coordination geometry is made by comparing the structure of $Co(Me_5dien)Cl_2$ and that of a related compound.

Introduction

Several X-ray structural investigations on five-coordinate transition metal complexes have been made in recent years in order to achieve some understanding of the factors which determine five-coordination.[1] In many cases the geometry of the ligand is found to be a major factor in stabilizing a given configuration, but even in these cases a structural analysis can provide useful information on the tendency of a metal atom toward a particular stereochemistry.

Ciampolini and Speroni[2] have reported the preparation and the physicochemical properties of a series of high-spin complexes with the general formula $M^{II}(Me_5dien)X_2$, where M is Mn, Fe, Co, Ni, Cu, or Zn, Me_5dien is the bulky ligand bis(2-dimethylaminoethyl)methylamine, $CH_3N(CH_2CH_2N(CH_3)_2)_2$, and X is Cl, Br, or I. From the molecular weight and conductivity measurements and on the basis of magnetic and spectral data a pentacoordinate structure was proposed for all the compounds in the series. An X-ray investigation was undertaken in this laboratory on the $Co(Me_5dien)Cl_2$ complex and preliminary results have been reported.[3] Here we wish to report the final results of the X-ray analysis of this compound. Recently, the structure of the high-spin five-coordinate complex $Co(Et_4dien)Cl_2$, with Et_4dien = bis(2-diethylaminoethyl)amine, has been determined.[4] This complex has the same set of donor atoms as $Co(Me_5dien)Cl_2$, but different substituents on the nitrogen atoms of the ligand molecule. For this reason, a somewhat different intramolecular crowding results in the two compounds and a comparison between the two structures appears interesting in order to elucidate the importance of steric factors in determining the coordination geometry about a metal atom.

Experimental Section

Data Collection.—Crystals of $Co[CH_3N(CH_2CH_2N(CH_3)_2)_2]Cl_2$, prepared as described earlier,[2] were kindly supplied by Dr. Ciampolini. The material crystallized as blue monoclinic plates, which were sensitive to moisture. For this reason the crystal used for data collection was coated with collodion. Cell parameters were determined by a least-squares refinement of 27 2θ values from $0kl$ and $h0l$ Weissenberg photographs taken with Fe Kα radiation and calibrated with NaCl (a = 5.6273 Å). The results are $a = 8.389 \pm 0.004$ Å, $b = 29.430 \pm 0.010$ Å, $c = 12.018 \pm 0.005$ Å, and $\beta = 101°\,31' \pm 4'$. A survey of hkl and $h0l$ Weissenberg photographs revealed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, which are consistent with the space group $P2_1/c$. The calculated density of 1.385 g cm^{-3}, for eight formula units in the unit cell, is in agreement with the observed value of 1.38 g cm^{-3} measured by flotation. No symmetry is imposed on the molecule by space group requirements and there are two independent molecules in the asymmetric unit.

The crystal used for data collection was a plate of approximate dimensions of 0.05 × 0.20 × 0.30 mm, coincident with the [010], [101], and [100] directions, respectively. Doubly integrated Weissenberg photographs $0kl$ through $5kl$ were taken on a Nonius camera with the multiple-film, equiinclination technique, using Fe Kα radiation (λ 1.9373 Å). The intensities of the reflections were measured on a Nonius microdensitometer, the intensity being assumed proportional to the density of the spot. The various levels were scaled by means of two Weissenberg photographs, containing 30° samples from each level, taken with the equiinclination technique. A total of 2533 independent reflections were examined but 966 of these were too weak to be measured. Intensities were corrected for Lorentz and polarization effects. With a calculated μ value of 93.0 cm^{-1} (Fe Kα) the transmission factors ranged from 0.29 to 0.64 over the set of reflections examined. A correction for absorption was applied, using Burnham's general absorption program, adapted by Stewart[5] for the "Crystal Structure Calculations System X-Ray 63." The atomic scattering factors for Co, Cl, N, and C were taken from the Dirac–Slater calculations by Cromer and Waber.[6] For H, the values tabulated in ref 7 were used. The real part of the anomalous dispersion correction, as given by Cromer,[8] was subtracted from f_{Co}.

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(1) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966); J. S. Wood, *Coord. Chem. Rev.*, **2**, 403 (1967).

(2) M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, **5**, 45 (1966).

(3) M. Di Vaira and P. L. Orioli, *Chem. Commun.*, 590 (1965).

(4) Z. Dori, R. Eisenberg, and H. B. Gray, *Inorg. Chem.*, **6**, 483 (1967).

(5) J. M. Stewart, Technical Report TR-64-6, University of Maryland Computer Science Center, 1964.

(6) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(7) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202.

(8) D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

TABLE I

FINAL ATOMIC COORDINATES[a] AND TEMPERATURE FACTORS[a-c] ($\times 10^4$)

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	487 (3)	932 (1)	3268 (2)	54 (5)	6 (1)	32 (2)	3 (1)	14 (2)	2 (1)
Cl(1)	2873 (6)	1312 (1)	3118 (3)	96 (11)	10 (1)	63 (3)	−12 (2)	28 (4)	−2 (1)
Cl(2)	741 (6)	823 (1)	5185 (3)	135 (10)	11 (1)	38 (3)	−2 (2)	19 (4)	4 (1)
N(1)	−1030 (22)	1502 (5)	2848 (11)	113 (44)	14 (2)	56 (13)	1 (7)	1 (15)	−1 (4)
N(2)	−1967 (17)	578 (4)	2819 (11)	135 (33)	9 (2)	60 (12)	11 (5)	26 (14)	−5 (4)
N(3)	1048 (16)	344 (4)	2387 (11)	67 (34)	9 (2)	71 (13)	−7 (5)	45 (15)	1 (4)
C(1)	−513 (26)	1874 (6)	3678 (18)	255 (51)	8 (2)	152 (22)	19 (8)	−37 (25)	−12 (6)
C(2)	−960 (28)	1673 (7)	1666 (15)	318 (59)	16 (3)	51 (15)	15 (10)	32 (22)	18 (5)
C(3)	−2760 (30)	1381 (7)	2884 (16)	179 (60)	16 (3)	92 (19)	21 (9)	7 (21)	9 (6)
C(4)	−3234 (25)	933 (8)	2310 (15)	160 (48)	24 (4)	71 (17)	8 (10)	−53 (20)	−10 (7)
C(5)	−2578 (26)	364 (7)	3799 (17)	164 (54)	20 (3)	103 (21)	−8 (10)	69 (25)	17 (6)
C(6)	−1831 (26)	234 (6)	1956 (17)	143 (50)	10 (2)	146 (22)	−6 (8)	16 (24)	−12 (6)
C(7)	−238 (30)	7 (5)	2318 (16)	387 (66)	6 (2)	101 (18)	−22 (9)	84 (27)	−15 (5)
C(8)	1406 (29)	469 (6)	1284 (17)	391 (59)	10 (2)	75 (18)	−13 (9)	101 (24)	−3 (5)
C(9)	2538 (26)	144 (6)	3067 (16)	177 (51)	11 (2)	118 (18)	25 (8)	38 (22)	0 (5)
Co(1)′	5288 (3)	3428 (1)	3174 (2)	132 (6)	8 (1)	35 (2)	1 (1)	13 (2)	−1 (1)
Cl(1)′	6535 (8)	4093 (2)	4030 (4)	365 (16)	15 (1)	70 (4)	−40 (2)	17 (6)	−3 (1)
Cl(2)′	6787 (7)	2852 (2)	4135 (4)	266 (14)	17 (1)	87 (4)	35 (2)	−48 (6)	−5 (1)
N(1)′	3152 (17)	3519 (4)	3841 (9)	167 (31)	8 (1)	27 (9)	17 (5)	2 (12)	−2 (3)
N(2)′	3527 (21)	2941 (4)	2008 (10)	176 (40)	5 (2)	65 (12)	5 (6)	22 (15)	−4 (3)
N(3)′	5959 (20)	3552 (5)	1619 (10)	28 (39)	18 (2)	62 (12)	−12 (6)	−1 (14)	−1 (4)
C(1)′	3536 (26)	3505 (6)	5094 (14)	335 (55)	15 (3)	31 (13)	13 (9)	61 (20)	5 (5)
C(2)′	2301 (27)	3956 (6)	3480 (16)	314 (55)	14 (2)	91 (18)	44 (9)	57 (23)	1 (5)
C(3)′	1989 (22)	3119 (6)	3469 (15)	90 (39)	15 (2)	94 (18)	−11 (7)	31 (19)	2 (5)
C(4)′	1926 (28)	3036 (6)	2197 (15)	148 (53)	14 (3)	75 (18)	−16 (9)	18 (21)	−12 (5)
C(5)′	3920 (25)	2457 (5)	2220 (16)	273 (48)	7 (2)	95 (18)	6 (7)	32 (22)	3 (5)
C(6)′	3688 (27)	3059 (5)	861 (14)	147 (53)	13 (2)	67 (16)	−2 (8)	41 (19)	−1 (5)
C(7)′	5327 (29)	3176 (6)	797 (13)	198 (53)	20 (3)	47 (14)	4 (10)	11 (20)	−10 (5)
C(8)′	5257 (26)	3986 (6)	1124 (14)	236 (49)	17 (3)	59 (15)	−9 (9)	24 (20)	11 (6)
C(9)′	7745 (36)	3578 (9)	1809 (16)	220 (78)	45 (6)	52 (17)	−6 (14)	43 (25)	3 (7)

[a] Estimated standard deviations (in parentheses) occur in the last significant digit; the calculated hydrogen positions are not reported. [b] Anisotropic thermal factors are of the form: $\exp(-\Sigma_{i=1}{}^3\Sigma_{j=1}{}^3 h_ih_j\beta_{ij})$. [c] Primed symbols denote atoms of the second molecule in the asymmetric unit.

Structure Determination.—The structure was solved by the heavy-atom technique, using the two independent cobalt atoms and a series of three-dimensional Fourier syntheses. At this point the R factor was 19.3%, assuming $B_{Co} = 2.5$ Å^2 and $B_{Cl} = B_N = B_C = 3.0$ Å^2. The residual R is defined throughout as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. Only observed reflections were included in the calculations.

A few cycles of block-diagonal least-squares refinement with individual isotropic temperature factors reduced R to 14.5%. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$; weights were calculated according to the function[9] $w = 1/(a + F_o + cF_o^2)$ where a and c were 40.0 and 0.08, respectively. Refinement was continued by means of full-matrix least-squares cycles, using the following weighting scheme: $w = 1$ for reflections with $F_o \leqslant 40$ and $\sqrt{w} = 40/F_o$ for reflections with $F_o > 40$. Two cycles of refinement on positional and thermal parameters and scale factors, with individual isotropic temperature factors, led to the value $R = 12.9\%$. A few errors made during data collection were corrected and hydrogens were introduced in calculated positions, assuming a C–H distance of 1.05 Å and $B_H = 5.0$ Å^2. One cycle of refinement on positional and anisotropic thermal parameters of the nonhydrogen atoms and one cycle on scale factors, followed by another cycle on positional and anisotropic thermal parameters, led to the final values for the residuals: $R = 8.2\%$ and $R_w = 10.5\%$, where R_w is defined as $(\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$.

During the last part of the refinement it appeared that high negative $F_o - F_c$ values for many strong, low-order reflections could be due to the effect of uncorrected secondary extinction. For this reason 10 reflections, considered to be affected by extinction, were omitted from the last cycles. A difference Fourier map calculated with the final parameters did not show any special features. The maximum height of the peaks was one-sixth the height of a carbon atom as found in another difference Fourier map calculated without the contribution of that carbon atom.

The final values of the parameters and their estimated standard deviations are reported in Table I. Standard deviations of the parameters were calculated according to the expression $\sigma_j = (\Sigma w(\Delta F)^2 a^{jj}/(m - n))^{1/2}$, where m is the number of reflections, n is the number of parameters refined, a^{jj} is the jjth element of the inverse matrix, and $\Delta F = F_o - F_c$. Table II reports the principal values of the thermal ellipsoids.

TABLE II

RMS DISPLACEMENTS (IN Å) ALONG THE PRINCIPAL AXES OF THE TEMPERATURE FACTOR ELLIPSOIDS[a]

Atom	Axis 1	Axis 2	Axis 3	Atom	Axis 1	Axis 2	Axis 3
Co(1)	0.127	0.146	0.174	Co(1)′	0.156	0.193	0.214
Cl(1)	0.153	0.213	0.229	Cl(1)′	0.178	0.241	0.390
Cl(2)	0.145	0.201	0.235	Cl(2)′	0.192	0.227	0.394
N(1)	0.181	0.219	0.247	N(1)′	0.134	0.147	0.269
N(2)	0.147	0.215	0.241	N(2)′	0.138	0.219	0.248
N(3)	0.101	0.204	0.233	N(3)′	0.080	0.214	0.287
C(1)	0.152	0.255	0.394	C(1)′	0.118	0.248	0.346
C(2)	0.132	0.285	0.342	C(2)′	0.151	0.249	0.378
C(3)	0.183	0.272	0.305	C(3)′	0.149	0.254	0.268
C(4)	0.147	0.280	0.352	C(4)′	0.170	0.231	0.286
C(5)	0.148	0.272	0.334	C(5)′	0.167	0.259	0.307
C(6)	0.183	0.229	0.333	C(6)′	0.188	0.235	0.246
C(7)	0.112	0.253	0.379	C(7)′	0.167	0.259	0.312
C(8)	0.184	0.203	0.376	C(8)′	0.176	0.267	0.308
C(9)	0.145	0.286	0.293	C(9)′	0.175	0.275	0.445

[a] Estimated standard deviations ($\times 10^3$) are about 10 for Co atoms, 20 for Cl atoms, and 30 for the lighter atoms.

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(9) D. W. J. Cruickshank, *et al.*, "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," Pergamon Press, Oxford, 1961, p 42.

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

0,K,0		
6	502	475
8	282	247
10	617	594
12	947	1113
14	560	582
16	1386	1592
18	893	849
20	818	849
22	440	442
24	350	274
28	370	407
0,K,1		
5	596	657
7	378	358
8	349	321
10	705	707
11	669	713
12	424	423
13	394	371
15	392	377
18	573	543
19	677	716
20	852	804
24	689	695
28	362	408
0,K,2		
2	210	217
3	965	1187
4	419	431
5	483	479
6	1022	1151
7	676	677
8	846	913
9	293	243
10	646	593
13	384	353
15	893	973
17	542	530
19	426	442
20	605	581
23	347	279
25	309	272
28	216	213
29	233	272
0,K,3		
1	270	285
2	1431E	1769
3	275	257
4	440	442
5	528	588
7	241	184
8	997	1062
9	992	1088
11	359	391
13	702	671
14	536	497
15	614	597
16	407	350
19	379	320
20	405	362
21	583	597
23	367	352
24	353	382
25	520	596
27	384	417
29	176	196
0,K,4		
0	749	788
1	845	900
2	452	415
3	1288	1581
4	515	497
5	1056	1173
8	281	246
10	496	470
11	625	638
13	506	450
14	421	361
16	464	459
19	386	352
27	315	308
0,K,5		
1	987	1136
3	295	306
4	525	475
5	1064	1171
6	437	398
7	1013	1107
8	1085	1183
9	896	942
12	689	636
15	499	513
17	685	676
19	385	352
20	397	370
21	348	310
22	326	247
23	647	702
24	453	454
25	278	282
27	393	390
0,K,6		
0	981	1028
3	370	304
4	1223	1392
5	670	622
6	322	249
9	693	685
10	397	366
11	414	385
12	789	754
13	413	347
16	491	500
0,K,7		
2	398	347
3	412	392
4	403	390
5	376	336
6	384	308
7	468	471
8	1061	1085
9	380	404
10	391	299
11	420	387
12	654	589
13	421	373
15	432	392
20	383	383
23	207	198
24	635	665
0,K,8		
0	738	787
2	455	417
4	570	573
6	436	418
11	406	369
13	444	444
15	455	403
16	377	306
21	206	200
0,K,9		
3	373	253
4	684	635
5	499	510
6	463	399
8	382	270
9	480	504
17	253	270
18	402	381
0,K,10		
0	684	739
1	595	614
3	561	603
7	405	457
9	379	340
13	367	334
14	331	323
15	496	509
0,K,11		
2	303	256
3	302	255
4	347	330
5	409	385
8	425	434
9	323	348
10	324	322
11	196	186
0,K,12		
0	501	462
1	276	299
1,K,0		
5	169	156
6	866	957
7	246	275
8	565	569
10	1041	1158
11	319	359
12	298	309
14	528	478
15	431	411
17	630	646
18	435	391
19	282	278
20	731	748
26	225	178
1,K,1		
3	293	385
4	387	393
5	1199E	1515
6	313	297
8	1391	1595
9	633	608
10	627	619
12	318	286
13	1108	1252
14	749	741
15	507	481
16	292	261
17	736	798
18	959	980
22	544	554
23	590	620
27	255	276
28	170	131
29	268	278
1,K,2		
0	501	448
1	280	259
2	127	98
3	518	511
4	1178	1294
5	661	743
6	438	437
7	892	994
8	853	925
9	1068	1145
10	930	918
11	1432	1609
12	536	468
13	271	343
14	319	258
15	693	662
16	427	355
17	323	343
18	291	237
19	501	499
20	290	267
21	286	267
22	320	347
23	448	460
25	350	353
27	389	396
29	191	211
1,K,3		
1	152	22
2	523	526
3	487	506
4	499	500
5	325	283
7	949	1048
8	773	781
9	600	601
10	372	327
11	281	288
12	581	557
13	398	324
15	749	813
21	353	379
23	304	316
24	382	379
26	206	170
28	255	260
1,K,4		
0	770	791
1	479	351
3	501	499
4	409	383
5	1276	1450
6	190	211
7	1204	1310
8	501	468
9	1095	1185
10	687	578'
11	620	593
12	262	208
13	329	274
14	378	338
15	630	644
19	634	661
21	553	546
22	438	386
25	500	477
26	446	502
27	198	202
1,K,5		
1	540	496
2	1125	1257
3	534	558
4	404	350
6	638	647
9	459	438
10	535	453
11	485	430
13	358	345
14	742	661
15	686	673
16	331	279
17	320	292
18	309	233
19	308	275
20	303	295
23	279	291
26	368	385
1,K,6		
0	474	494
1	768	765
2	629	604
3	651	607
6	1371	1449
7	419	354
9	488	470
10	1420	1410
11	280	203
12	342	243
14	462	469
15	416	370
18	462	445
20	278	304
21	236	228
22	640	738
24	159	174
25	185	178
1,K,7		
1	371	328
2	771	792
3	288	210
4	723	640
5	335	308
6	261	194
7	503	478
14	574	516
15	343	283
18	595	618
19	243	272
20	220	217
21	211	196
22	193	246
1,K,8		
0	962	982
2	485	486
3	325	290
6	452	457
7	520	528
8	276	271
10	284	274
11	593	597
14	309	245
19	190	179
21	196	237
1,K,9		
1	603	577
2	535	515
3	398	346
5	399	388
8	550	515
9	385	390
10	483	459
11	309	275
13	270	202
14	461	477
15	336	327
16	221	262
17	286	289
18	216	222
1,K,10		
0	605	702
3	350	382
4	293	328
5	275	243
7	321	331
9	424	357
1,K,11		
1	272	302
2	589	639
4	190	215
5	201	235
8	316	311
1,K,-1		
4	192	193
5	200	197
6	342	315
7	874	1005
8	948	993
9	451	459
10	705	700
11	854	911
12	345	333
13	695	690
14	1358	1443
16	481	437
17	586	577
18	1189	1205
19	283	200
23	272	251
24	290	248
26	354	392
29	263	250
1,K,-2		
0	242	234
1	154	118
2	644	722
3	698	755
4	648	680
5	212	228
6	841	798
7	351	355
8	894	954
9	773	810
10	631	604
13	523	491
14	500	485
15	270	215
16	319	309
17	281	195
19	350	330
22	610	582
23	532	512
24	426	423
26	261	303
1,K,-3		
1	510	517
2	299	232
3	910	1041
5	286	292
6	494	496
7	761	768
8	611	606
9	218	230
10	320	285
11	678	647
13	701	690
14	373	330
15	750	745
16	316	296
17	650	602
19	932	963
21	350	310
26	308	289
27	328	355
28	203	242
29	208	268
1,K,-4		
0	1610E	2220
1	433	375
2	679	745
3	830	877
4	751	737
5	833	909
6	409	364
7	1205	1331
8	450	422
9	985	951
10	748	772
11	263	287
14	620	513
16	465	386
18	403	387
19	467	430
20	374	337
22	404	385
23	639	655
24	236	229
25	294	297
27	193	205
1,K,-5		
1	1045	1158
2	817	844
3	830	810
5	999	1127
6	368	343
8	618	622
9	592	585
10	749	743
11	548	499
13	838	818
14	846	772
15	362	303
17	481	458
18	708	697
19	300	244
21	338	357
22	257	252
25	241	241
27	240	271
1,K,-6		
0	726	773
1	482	464
2	269	229
3	540	503
4	262	261
5	556	580
6	1203	1364
7	858	851
8	731	723
9	576	578
10	1044	1070
11	429	392
12	530	539
16	332	268
18	354	294
19	290	228
21	254	273
22	344	326
23	279	310
25	431	465
26	180	202
1,K,-7		
3	504	526
6	590	551
7	877	917
8	482	458
10	627	610
11	698	694
12	321	245
14	686	682
16	347	304
18	377	347
20	244	220
22	214	206
1,K,-8		
0	368	313
6	788	834
10	770	774
14	328	277
15	314	268
17	332	343
20	259	267
22	350	366
1,K,-9		
2	860	917
10	329	319
12	303	242
14	531	556
15	302	373
18	347	345
19	348	410
1,K,-10		
2	383	333
3	535	527
5	635	673
6	303	252
7	429	416
9	716	751
11	311	339
13	403	410
16	259	287
1,K,-11		
1	523	585
3	247	214
5	283	253
10	226	236
11	184	187
13	383	506
1,K,-12		
1	389	369
2	177	190
5	210	251
2,K,0		
4	424	631
5	793	903
6	262	233
7	696	742
8	596	625
9	1206	1371
12	1639	1863
13	768	804
14	406	365
15	749	795
16	817	783
17	683	659
19	473	454
20	399	358
21	440	440
25	235	218
26	319	362
27	189	183
28	226	243
2,K,1		
2	347	388
3	475	552
4	463	406
5	869	951
6	919	996
7	1430	1615
8	1541E	1938
9	783	835
11	1062	1136
12	917	943
13	512	461
14	308	274
15	443	420
16	285	272
17	689	642
18	478	410
21	480	463
23	369	317
24	361	340
25	249	224
2,K,2		
0	892	1057
1	464	481
5	720	780
6	697	735
7	453	450
8	213	225
10	939	1014
11	541	498
13	829	836
17	680	722
18	546	342
19	465	475
20	327	311
21	345	312
25	292	291
26	318	318
27	273	283
2,K,3		
3	459	486
4	266	250
5	711	812
6	236	258
7	1602E	1930
9	1258	1321
10	386	374
11	1125	1247
13	530	464
15	740	732
17	564	514
21	331	372
22	276	277
23	459	463
24	339	333
25	453	468
2,K,4		
1	501	528
3	427	397
4	382	385
7	257	243
9	778	808
11	347	333
12	734	649
13	602	735
14	480	444
15	736	678
17	513	525
19	405	388
20	282	247
23	287	289
2,K,5		
1	589	581
2	622	609
3	755	846
4	851	954
6	256	214
7	264	238
8	1509	1608
10	713	717
11	321	361
12	795	791
13	345	341
14	636	607
19	434	377
20	649	640
24	493	527
2,K,6		
0	784	793
1	304	286
2	306	281
3	328	341
4	313	297
7	288	235
8	295	226
11	334	284
12	596	557
16	854	877
17	537	528
20	472	510
2,K,7		
1	309	289
2	959	1005
4	547	523
5	449	410
7	464	474
8	441	466
9	451	409
11	451	428
12	743	775
14	326	321
16	472	478
18	283	288
20	251	238
21	334	347
22	173	189
2,K,8		
0	522	442
1	413	411
4	296	119
8	302	231
12	483	471
15	298	281
16	492	550
17	431	473
19	187	196
2,K,9		
2	351	332
3	392	376
5	279	259
6	279	197
7	445	453
8	403	361
9	273	227
11	472	464
13	223	203
2,K,10		
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1	244	254
3	454	485
4	241	209
6	235	232
7	231	201
9	315	333
10	240	243
11	365	399
2,K,11		
1	159	190
2	180	246
3	159	185
4	340	441
2,K,-1		
4	348	495
6	234	216
7	508	629
8	1261	1458
9	302	313
10	804	839
11	570	589
12	819	805
13	488	477
14	433	416
18	320	302
20	554	572
24	254	199
29	113	169
2,K,-2		
2	496	715
3	191	154
4	176	132
5	306	275
6	228	216
7	193	177
8	293	230
9	494	451
10	817	786
11	792	766
12	1045	1088
13	366	339
15	497	464
16	1315	1429
18	416	369
20	684	672
23	266	264
27	245	245
28	212	199
2,K,-3		
1	790	814
2	1024	1112
3	733	753
4	473	481
5	252	260
7	434	390
8	380	311
9	303	280
11	542	475
12	762	726
13	612	643
16	411	351
17	298	250
20	337	308
21	587	601
23	325	324
25	330	368
28	142	165
2,K,-4		
0	404	321
1	1259	1400
2	408	369
3	428	407
4	264	229
7	255	223
9	697	718
10	257	203
11	461	391
12	685	658
13	819	755
15	892	853
16	361	359
17	1084	1151
19	575	556
21	527	530
24	231	271
25	208	180
2,K,-5		
1	331	314
2	200	154
3	1258	1390
5	1013	1086
6	434	425
7	1218	1382
8	245	224
9	529	511
11	931	914
14	415	368
15	398	347
17	319	284
19	299	288
21	355	351
22	253	251
23	288	332
2,K,-6		
0	963	1045
1	450	407
2	277	231
3	382	353
4	731	755
5	540	471
6	760	751
8	616	559
9	369	330
10	380	359
11	554	495
12	826	772
13	683	659
15	485	402
16	914	895
17	475	478
19	461	463
21	492	482
24	180	173
25	203	224
2,K,-7		
1	728	748
2	392	381
3	421	438
4	674	692
7	708	683
8	997	991
9	704	622
11	427	412
12	420	397
14	343	250
15	356	302
18	336	341
20	333	303
24	317	331
2,K,-8		
0	304	258
1	305	241
3	348	321
4	465	513
5	377	329
6	527	492
2,K,-8		
6	527	492
10	453	477
12	551	515
14	488	405
16	636	658
18	353	331
20	444	501
2,K,-9		
3	276	330
4	746	743
6	374	282
8	942	959
9	307	252
10	308	[illegible]
12	440	435
13	317	275
14	298	265
18	293	332
20	214	252
2,K,-10		
6	308	257
8	442	463
11	274	194
12	519	529
13	240	240
15	293	307
16	443	506
3,K,0		
2	127	107
3	609	679
4	251	257
5	1212E	1679
6	1049	1290
7	504	610
8	476	442
9	767	872
10	1112	1196
11	414	364
13	407	391
14	506	465
16	298	343
18	576	518
19	548	539
21	308	261
22	690	687
24	287	284
25	286	275
26	422	460
27	148	135
3,K,1		
1	737	709
2	368	355
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5	538	591
6	907	971
8	607	614
9	544	529
10	360	204
11	378	372
14	315	307
15	768	785
16	320	294
17	423	403
21	325	335
22	273	275
23	237	193
25	197	209
27	135	151
3,K,2		
0	215	172
1	184	162
3	495	480
5	1011	1074
7	759	831
8	601	556
9	432	385
11	904	867
13	382	363
16	633	630
17	294	232
18	289	241
19	459	440
20	305	256
21	540	489
23	469	481
24	207	173
25	365	394
27	302	411
3,K,3		
1	674	761
2	364	380
3	695	736
8	404	339
9	256	185
10	445	425
12	375	409
15	364	353
16	596	588
17	473	466
18	290	253
19	278	178
20	265	249
22	348	335
25	160	156
3,K,4		
0	219	201
1	220	180
2	377	318
3	675	698
5	289	304
6	1078	1084
7	449	440
8	527	488
10	770	734
12	406	348
16	439	458
17	688	704
18	327	281
21	560	596
22	441	457
3,K,5		
1	349	311
2	970	974
3	536	505
5	261	209
8	654	609
9	290	177
10	643	600
11	387	341
14	750	650
18	522	510
21	270	274
23	156	163
3,K,6		
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1	270	225
2	417	381
3	551	567
5	420	351
6	478	445
7	453	398
9	745	725
10	290	379
11	421	343
13	461	435
14	366	352
15	494	503
16	472	395
17	273	290
19	236	332
22	268	327
3,K,7		
1	291	204
2	591	559
3	205	258
4	307	258
6	288	247
7	465	397
11	478	444
12	355	301
14	272	230
15	361	373
18	337	318
19	439	431
3,K,8		
1	401	401
5	285	290
6	475	454
7	285	312
9	341	353
10	459	443
12	438	429
15	193	196
16	299	290
3,K,9		
1	546	588
3	378	363
5	430	440
6	241	243
8	426	482
11	408	497
12	338	326
13	406	512
3,K,10		
0	188	199
5	327	350
6	302	258
7	256	316
3,K,-1		
4	321	310
5	514	578
6	920	1080
7	681	795
9	461	442
10	938	1000
11	238	216
12	246	199
13	371	316
14	993	971
15	786	803
17	510	497
18	387	326
19	387	388
20	435	412
21	309	301
25	206	181
26	381	399
3,K,-2		
0	599	821
1	728	987
2	469	538
3	760	1022
5	226	206
6	956	1073
7	486	517
8	374	339
9	306	300
10	1002	1008
11	250	277
14	486	410
15	625	628
17	303	292
21	465	470
22	565	563
25	281	307
26	467	518
3,K,-3		
1	746	871
2	991	1215
3	768	895
4	407	424
6	266	258
7	772	845
8	562	573
10	334	304
13	282	226
14	888	868
15	288	215
16	288	232
17	287	250
18	897	1008
22	252	206
24	217	181
26	168	175
3,K,-4		
0	466	425
1	816	925
2	521	476
3	173	132
5	190	186
6	748	766
7	455	427
8	293	282
10	540	484
11	839	848
12	664	580
15	529	454
17	342	339
21	310	325
22	350	341
23	342	366
25	237	268
27	157	185
3,K,-5		
1	1160	1390
2	198	153
3	988	1061
4	216	225
5	816	917
7	234	204
8	430	354
9	482	461
10	653	604
11	648	654
13	835	793
15	680	644
17	967	1074
19	356	322
23	224	220
3,K,-6		
0	402	335
1	486	483
2	424	416
3	350	346
4	392	361
5	532	508
6	268	255
7	791	843
8	393	386
9	764	824
11	393	360
13	530	467
17	352	341
18	535	511
21	535	591
23	207	209
25	183	189
3,K,-7		
1	335	286
2	1212	1422
3	384	344
6	392	404
7	508	454
14	742	700
15	314	265
17	278	255
18	451	442
19	344	367
20	226	208
23	258	297
3,K,-8		
6	642	646
7	291	284
8	295	230
9	437	451
10	508	486
11	309	255
12	418	338
14	311	269
18	222	222
3,K,-9		
1	445	484
2	556	616
3	448	458
6	465	462
7	347	362
8	371	328
14	444	446
16	275	229
18	334	346
19	159	180
3,K,-10		
6	665	684
7	402	430
10	489	495
11	258	223
12	239	202
16	224	267
4,K,0		
1	584	740
2	187	204
3	1083E	1488
4	472	528
5	306	313
6	438	507
7	240	266
8	390	332
9	214	200
11	525	572
13	301	307
15	620	644
18	225	178
19	417	364
20	211	181
25	132	161
4,K,1		
1	619	656
2	751	801
3	546	538
4	144	137
5	705	707
7	828	870
8	362	410
9	770	901
10	366	305
12	242	176
13	547	543
14	568	488
18	398	354
19	434	414
21	327	300
23	499	560
25	477	463
4,K,2		
0	422	386
1	850	888
2	236	225
3	462	464
4	165	176
5	428	477
7	336	323
9	605	580
10	345	332
14	366	341
15	247	236
17	388	401
19	261	249
20	209	163
21	331	308
25	172	214
4,K,3		
1	406	402
2	582	588
3	578	612
4	417	436
5	593	599
6	200	187
7	216	201
8	573	617
10	239	177
12	339	296
13	448	388
15	250	225
18	258	220
19	722	769
20	378	346
21	237	255
23	313	280
24	353	392
4,K,4		
0	1424	1487
1	708	755
3	340	339
4	761	696
6	460	479
10	326	341
12	486	409
15	405	367
16	669	613
20	204	229
4,K,5		
1	416	383
2	263	288
4	742	783
5	514	494
6	371	340
7	386	372
8	428	368
11	554	566
13	336	275
15	398	361
16	266	249
17	228	218
18	228	225
20	560	573
4,K,6		
0	811	841
1	516	487
3	468	416
4	467	397
7	420	392
9	320	318
15	440	445
16	218	234
17	267	272
19	234	255
4,K,7		
5	262	283
8	309	290
9	221	183
10	323	350
13	258	267
14	307	327
4,K,8		
1	470	494
3	444	472
4	288	278
5	312	315
6	197	186
7	194	186
10	379	403
12	142	195
13	255	308
4,K,9		
1	212	204
5	313	294
6	193	203
7	394	397
4,K,-1		
2	519E	879
3	227	238
4	627	822
5	261	279
7	614	742
8	1425E	1753
9	520	557
11	295	309
12	516	468
13	504	494
16	595	585
20	624	612
22	308	289
24	751	791
25	136	156
26	161	186
4,K,-2		
0	638	863
1	265	315
2	414	487
4	930	1176
5	252	243
7	436	397
8	512	451
10	272	258
11	232	234
12	722	753
14	399	339
16	405	369
17	289	272
19	228	177
20	269	260
22	245	247
23	174	162
25	155	137
4,K,-3		
2	255	211
3	344	361
4	330	308
5	354	345
6	554	583
7	384	379
8	752	760
9	715	737
10	462	383
12	539	506
14	611	548
20	258	165
22	232	204
23	397	433
24	678	712
25	196	184
4,K,-4		
0	1054	1196
1	824	789
3	342	341
4	682	758
5	814	848
6	490	481
7	187	185
9	489	482
10	433	398
11	265	231
12	546	458
13	306	281
14	294	248
15	468	407
16	331	330
17	281	227
19	267	276
21	227	213
22	413	424
24	258	247
25	140	156
4,K,-5		
1	167	138
2	484	439
3	239	221
4	537	545
5	763	731
6	370	321
7	243	241
8	501	475
9	714	767
10	383	355
11	525	515
13	440	381
19	531	549
20	217	192
21	326	329
23	318	329
5,K,-8		
3	339	346
5	299	273
6	431	414
7	239	209
10	227	164
11	237	231
14	234	259
16	186	199
5,K,-9		
12	244	293
4,K,-5		
24	230	198
4,K,-6		
0	396	340
1	1117	1276
3	940	1028
5	311	287
7	746	752
9	388	310
11	272	200
12	261	223
13	357	366
15	915	1018
16	512	463
18	233	245
19	426	487
4,K,-7		
1	268	209
4	541	556
5	613	617
8	362	363
9	513	547
12	373	339
13	325	303
16	221	208
19	416	418
20	376	375
21	257	303
4,K,-8		
0	788	839
1	223	200
4	563	598
8	238	205
9	242	257
11	247	229
12	248	210
15	210	196
16	543	610
20	162	189
4,K,-9		
2	341	350
4	225	183
5	389	376
7	228	213
8	377	355
10	350	302
12	367	335
17	209	234
4,K,-10		
12	301	327
5,K,0		
0	605	806
2	120	88
3	658	848
4	641	665
5	612	711
7	952	1112
9	757	775
10	228	251
11	352	296
13	523	507
14	241	219
15	536	488
16	538	478
19	189	219
21	429	460
23	321	351
24	200	221
5,K,1		
1	484	544
2	569	556
3	887	773
4	232	227
6	634	612
7	288	277
13	339	325
15	308	257
16	338	302
17	521	506
19	526	554
20	407	415
21	183	172
23	179	176
5,K,2		
0	611	596
1	666	677
3	176	184
4	547	483
5	576	572
6	320	320
7	329	296
8	413	359
9	574	534
10	441	376
11	250	259
13	482	480
15	419	418
16	380	333
21	138	166
22	444	440
5,K,3		
1	512	525
2	811	815
3	326	289
6	439	369
7	384	343
9	295	245
13	678	652
14	459	392
15	366	347
17	464	452
18	391	482
19	276	295
5,K,4		
0	238	219
1	351	354
2	540	545
3	235	242
4	347	327
5	507	464
6	667	621
7	257	212
9	398	398
10	517	440
15	235	269
18	498	521
5,K,5		
1	552	513
2	648	640
3	327	291
5	427	413
9	495	450
10	342	272
13	281	259
14	598	659
17	404	394
18	342	379
5,K,6		
3	335	354
4	274	277
7	291	258
10	293	241
11	195	198
12	356	375
13	182	208
5,K,7		
1	321	333
2	223	243
3	276	390
5	186	214
7	350	373
8	316	318
10	157	197
5,K,8		
4	220	251
5	160	177
6	105	127
5,K,-1		
3	310	413
4	325	374
5	487	648
10	613	617
11	513	487
12	243	220
13	245	237
14	681	736
17	331	319
18	450	363
19	221	236
20	282	289
21	192	167
22	162	153
5,K,-2		
2	132	220
3	210	280
4	211	172
5	474	507
6	915E	1222
7	196	159
8	300	280
9	429	441
10	1100	1235
11	279	267
12	282	274
18	201	192
19	214	230
20	188	219
22	433	459
23	260	249
5,K,-3		
1	112	150
[illegible]	162	107
5	179	160
6	260	310
8	215	172
9	550	518
10	388	378
13	284	293
14	530	490
16	299	285
18	231	169
19	257	264
22	260	291
23	277	279
5,K,-4		
0	250	208
1	418	441
2	259	251
3	341	373
5	589	645
6	523	608
7	297	261
8	212	177
9	631	631
10	629	568
11	382	403
17	350	377
20	309	305
22	299	305
23	185	228
5,K,-5		
1	332	366
2	1007	1116
3	176	194
4	238	234
5	286	259
6	310	280
8	453	447
9	280	264
10	361	344
11	439	413
13	546	473
14	529	495
15	555	521
17	290	245
19	335	336
20	280	249
21	138	163
5,K,-6		
3	557	568
5	711	783
7	465	445
9	817	813
11	322	271
13	496	437
16	312	293
19	274	302
21	211	264
5,K,-7		
1	671	734
2	256	232
3	263	253
4	269	234
5	233	198
6	350	372
7	337	352
8	273	238
10	515	469
11	366	353
14	488	442
15	418	400
17	353	397
18	289	293
19	233	261

[a] Columns are K, $10F_o$, and $10F_c$. Reflections considered affected by extinction are marked with an E and were omitted from final refinement.

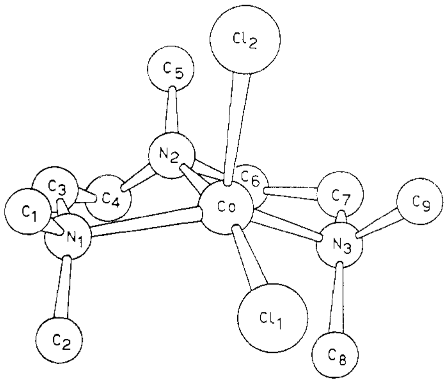

Figure 1.—A perspective view of the molecule of Co(Me_5dien)Cl_2. The numbering of the two chlorine atoms has been interchanged with respect to that adopted in the previous note,[3] in order to make the comparison with the structure of Co(Et_4dien)Cl_2 easier.

The computer programs used in the calculations were those written for the IBM 1620 by Albano, Bellon, Pompa, and Scatturin[10] and those of the "Crystal Structure Calculations System," written by Stewart, *et al.*,[5] for the IBM 709/7090/7094. The observed and calculated structure factors are reported in Table III.

Discussion

The structure consists of discrete molecules of Co(Me_5dien)Cl_2. In the two crystallographically independent molecules only a few of the corresponding bond lengths and angles show statistically significant differences. Since these differences are unimportant to the following discussion, values quoted hereafter for bond distances and angles are the average between those for the two independent molecules, unless otherwise indicated. A perspective view of the molecule is shown in Figure 1. Tables IV and V report intramolecular distances and angles.

Table IV
Bond Lengths and Intramolecular Contacts

	Distance, Å	
Atoms	Molecule 1	Molecule 2
Co–Cl(1)	2.331 (6)	2.358 (6)
Co–Cl(2)	2.294 (5)	2.282 (6)
Co–N(1)	2.105 (16)	2.121 (15)
Co–N(2)	2.274 (14)	2.317 (14)
Co–N(3)	2.129 (14)	2.089 (15)
N(1)–C(1)	1.49 (2)	1.48 (2)
N(1)–C(2)	1.52 (2)	1.49 (2)
N(1)–C(3)	1.50 (3)	1.54 (2)
N(2)–C(4)	1.53 (3)	1.43 (3)
N(2)–C(5)	1.51 (3)	1.47 (2)
N(2)–C(6)	1.47 (2)	1.45 (2)
N(3)–C(7)	1.45 (3)	1.51 (2)
N(3)–C(8)	1.46 (3)	1.48 (2)
N(3)–C(9)	1.47 (2)	1.47 (3)
C(3)–C(4)	1.51 (3)	1.54 (3)
C(6)–C(7)	1.48 (3)	1.43 (4)
Cl(1)···C(1)	3.47 (2)	3.50 (2)
Cl(1)···C(2)	3.50 (2)	3.50 (2)
Cl(1)···C(8)	3.38 (2)	3.46 (2)
Cl(1)···C(9)	3.45 (2)	3.40 (2)
Cl(2)···C(5)	3.24 (2)	3.20 (2)

Table V
Bond Angles

	Angle, deg	
Atoms	Molecule 1	Molecule 2
Cl(1)–Co–Cl(2)	103.6 (0.2)	104.1 (0.2)
Cl(1)–Co–N(1)	94.9 (0.5)	93.7 (0.4)
Cl(1)–Co–N(2)	162.2 (0.4)	162.0 (0.4)
Cl(1)–Co–N(3)	94.2 (0.4)	94.0 (0.4)
Cl(2)–Co–N(1)	106.4 (0.4)	109.0 (0.4)
Cl(2)–Co–N(2)	94.1 (0.4)	93.9 (0.4)
Cl(2)–Co–N(3)	113.6 (0.4)	111.2 (0.5)
N(1)–Co–N(2)	80.3 (0.6)	79.8 (0.6)
N(1)–Co–N(3)	135.3 (0.5)	135.6 (0.6)
N(2)–Co–N(3)	77.8 (0.5)	79.6 (0.6)
Co–N(1)–C(1)	110.2 (1.1)	110.7 (1.2)
Co–N(1)–C(2)	110.8 (1.3)	113.0 (1.2)
Co–N(1)–C(3)	110.2 (1.1)	109.1 (1.0)
C(1)–N(1)–C(2)	108.8 (1.5)	108.3 (1.3)
C(1)–N(1)–C(3)	108.0 (1.6)	105.8 (1.3)
C(2)–N(1)–C(3)	108.9 (1.5)	109.7 (1.3)
Co–N(2)–C(4)	107.9 (1.1)	106.8 (1.0)
Co–N(2)–C(5)	115.9 (1.0)	113.5 (1.1)
Co–N(2)–C(6)	106.8 (1.2)	104.9 (1.1)
C(4)–N(2)–C(5)	106.3 (1.5)	110.1 (1.5)
C(4)–N(2)–C(6)	109.5 (1.3)	111.8 (1.5)
C(5)–N(2)–C(6)	110.4 (1.4)	109.6 (1.4)
Co–N(3)–C(7)	110.3 (1.2)	109.6 (1.2)
Co–N(3)–C(8)	110.5 (1.0)	110.7 (1.2)
Co–N(3)–C(9)	107.2 (1.0)	108.6 (1.1)
C(7)–N(3)–C(8)	113.8 (1.4)	108.1 (1.3)
C(7)–N(3)–C(9)	107.3 (1.4)	110.8 (1.7)
C(8)–N(3)–C(9)	107.3 (1.6)	109.1 (1.7)
N(1)–C(3)–C(4)	111.2 (1.9)	107.8 (1.5)
N(2)–C(4)–C(3)	108.4 (1.5)	110.0 (1.5)
N(2)–C(6)–C(7)	107.2 (1.5)	112.3 (1.6)
N(3)–C(7)–C(6)	109.0 (1.4)	110.9 (1.8)

The cobalt atom is in a five-coordinate environment, surrounded by two chlorine and three nitrogen atoms. The coordination configuration appears to be intermediate between the two idealized geometries for five-coordination: the trigonal bipyramid and the square pyramid. From the trigonal-bipyramidal viewpoint Cl(1) and N(2) occupy the axial positions. The metal atom is shifted by 0.26 Å toward Cl(1), out of the equatorial plane defined by Cl(2), N(1), and N(3). In the square-pyramidal approximation Cl(2) should be considered to occupy the apical position with the metal atom 0.55 Å above the base. The equations of the least-squares planes are reported in Table VI.

Large distortions with respect to both geometries are imposed by the steric requirements of the ligands. The situation is similar in some respects to that found in the structure of the compound Co(Et_4dien)Cl_2.[4] The differences between Co(Me_5dien)Cl_2 and Co(Et_4dien)Cl_2 can be ascribed essentially to the intramolecular crowding, which is different for the two compounds. Figure 2 shows schematic drawings of the coordination polyhedra of the two compounds.

Replacement of methyl groups with the bulkier ethyl groups might be expected to lead to an increase in nonbonded repulsions. In spite of this, shorter intramolecular contacts are found in Co(Me_5dien)Cl_2 than in the other complex. This is due to the presence of a total of five substituent groups on the nitrogen atoms in the ligand Me_5dien, compared with the four sub-

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(10) (a) V. Albano, P. L. Bellon, and F. Pompa, *Ric. Sci. Suppl.*, **33**, 285 (1963); (b) V. Albano, P. L. Bellon, F. Pompa, and V. Scatturin, *ibid.*, **33**, 1067 (1963).

TABLE VI

BEST PLANES WITH DEVIATIONS OF ATOMS FROM THE PLANES

Equations of the Planes[a]

Plane	Atoms	*A*	*B*	*C*	*D*
1	Cl(2), N(1), N(3), Co[b]	7.387	13.878	−1.564	0.878
1′	Cl(2)′, N(1)′, N(3)′, Co′[b]	3.633	21.962	4.913	10.761
2	Cl(1), N(1), N(2), N(3), Co[b]	−0.110	−4.784	11.650	2.804
2′	Cl(1)′, N(1)′, N(2)′, N(3)′, Co′[b]	−4.197	20.183	−5.023	3.661
3	Co, Cl(1), Cl(2), N(2), C(5)[b]	−4.026	25.742	1.957	2.835
3′	Co′, Cl(1)′, Cl(2)′, N(2)′, C(5)′[b]	−6.282	−0.454	9.600	−0.424

Plane 1		Plane 2		Plane 3	
Atoms	Dev, Å	Atoms	Dev, Å	Atoms	Dev, Å
Cl(2)		Cl(1)	−0.17	Co	−0.01
N(1)		N(1)	0.19	Cl(1)	0.00
N(3)		N(2)	−0.22	Cl(2)	0.00
Co[b]	−0.26	N(3)	0.20	N(2)	0.00
		Co[b]	−0.55	C(5)[b]	0.12

Plane 1′		Plane 2′		Plane 3′	
Atoms	Dev, Å	Atoms	Dev, Å	Atoms	Dev, Å
Cl(2)′		Cl(1)′	0.17	Co′	0.01
N(1)′		N(1)′	−0.19	Cl(1)′	0.00
N(3)′		N(2)′	0.21	Cl(2)′	0.00
Co′[b]	−0.25	N(3)′	−0.19	N(2)′	0.00
		Co′[b]	0.56	C(5)′[b]	0.02

Planes	Dihedral angle, deg	Planes	Dihedral angle, deg
1–2	87.6	1′–2′	88.4
1–3[c]	89.6	1′–3′[c]	89.9
2–3[d]	86.1	2′–3′[d]	89.2

[a] The equations of the planes are $Ax + By + Cz = D$ in monoclinic fractional coordinates. [b] Atoms not included in the calculation of the planes (weight zero). [c,d] The corresponding dihedral angles in the molecule Co(Et$_4$dien)Cl$_2$ are 87.7 and 78.4°, respectively.

stituents in Et$_4$dien. The presence of the methyl group attached to the central nitrogen atom in Co(Me$_5$dien)Cl$_2$ plays an important role in determining the details of the molecular conformation in that complex.

The very short Cl(2)···C(5) contact of 3.22 Å in Co(Me$_5$dien)Cl$_2$ (the sum of the van der Waals radii of chlorine and methyl carbon is about 3.80 Å) is indicative of crowding due to steric hindrance. Clear evidence for this is provided by the unusually high values of the Co–N(2)–C(5) angle (115°) and the Co–N(2) bond length (2.29 Å). Moreover, the Cl(2)–Co–N(2) angle, which is 83.3° in Co(Et$_4$dien)Cl$_2$, reaches a value of 94.0° in Co(Me$_5$dien)Cl$_2$. Displacement of the ligand molecule as a whole away from Cl(2) does not completely release the strains caused by the short Cl(2)···C(5) contact, because additional short contacts obtain at the two ends of the chain between the other four methyl groups and Cl(1). The average value of these nonbonded distances is 3.45 Å, which is smaller than the average (3.51 Å) of the chlorine–carbon contacts in Co(Et$_4$dien)Cl$_2$. In the latter only distances shorter than 3.60 Å were included. From all this evidence we assume that steric hindrance is greater in Co(Me$_5$dien)Cl$_2$ than in Co(Et$_4$dien)Cl$_2$. This conclusion is the reverse of that stated by Dori, Eisenberg, and Gray.[4]

In this connection we want to point out that the coordination configuration in Co(Me$_5$dien)Cl$_2$ is more distorted than that of Co(Et$_4$dien)Cl$_2$ and can be less adequately described in terms of a regular idealized geometry. Although Dori, *et al.*, refer to a distorted square pyramid with Cl(2) in the apical position for Co(Et$_4$dien)Cl$_2$, we believe that a description in terms of a distorted trigonal bipyramid with Cl(1) and N(2) in the axial positions is more suitable for that compound. Our viewpoint is supported by the fact that the atoms Cl(1), Co, and N(2) in Co(Et$_4$dien)Cl$_2$ are almost collinear: the angle Cl(1)–Co–N(2) is 173.4°. The three angles in the equatorial plane measure 120.4, 126.8, and 105.9°, respectively. The mean angular deviation from the regular trigonal bipyramid in the coordination polyhedron of Co(Et$_4$dien)Cl$_2$ is 8.1°, while the mean deviation from the square pyramid[11] is 13.5°. In the case of Co(Me$_5$dien)Cl$_2$ these deviations amount to 10.1 and 8.3°, respectively. The above figures support the idea that, although both polyhedra are rather distorted, the Co(Me$_5$dien)Cl$_2$ polyhedron is almost intermediate between the two ideal geometries (possibly favoring the square pyramid) whereas the Co(Et$_4$dien)Cl$_2$ polyhedron is closer to a trigonal bipyramid. The tendency toward a more regular arrangement is shown by that complex which is less hindered. This may be the result of a bias to adopt that configuration which minimizes the electrostatic repulsions between the negatively charged ligand atoms, which is the trigonal bipyramid.[12]

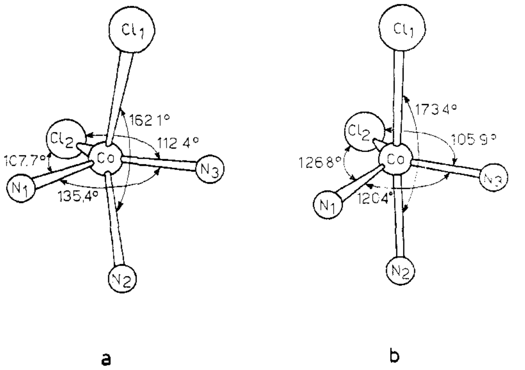

Figure 2.—Schematic drawing of the coordination polyhedra of Co(Me$_5$dien)Cl$_2$ (a) and of Co(Et$_4$dien)Cl$_2$ (b).

No other factors should be as effective in determining the differences between the two complexes as the steric repulsions considered so far. Neither the electronic factors, which may undergo slight changes in going from Me$_5$dien to Et$_4$dien, nor crystal packing can substantially affect the conformation of these compact and overcrowded molecules. The last point is supported by the fact that the two crystallographically independent molecules in Co(Me$_5$dien)Cl$_2$ are essentially identical.

The large value of the Co–N(2) distance has already been rationalized in terms of the Cl(2)···C(5) crowding. The other two cobalt–nitrogen distances average 2.11 ± 0.02 Å, which is considerably less than the value of 2.20 Å found in Co(Et$_4$dien)Cl$_2$. This shorten-

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(11) The ideal model of square pyramid chosen by H. Montgomery and E. C. Lingafelter, *Acta Cryst.*, **16**, 748 (1963), has been adopted in order to calculate the mean angular deviations reported here.

(12) J. Zemann, *Z. Anorg. Allgem. Chem.*, **324**, 241 (1963).

ing may well be due to the decrease in ligand–ligand repulsions which follows from the elongation of the central cobalt–nitrogen bond. In spite of the large range of values for individual distances, the average of 2.17 ± 0.09 Å for the three cobalt–nitrogen bond lengths compares well with the corresponding value of 2.19 Å for $Co(Et_4dien)Cl_2$. Similarly, the intrachelate N···N distances average to 2.82 Å in both compounds. The intrachelate N–Co–N angles average to 79.3 ± 1.1°, close to the value of 80.3° found in $Co(Et_4dien)Cl_2$.

The N(1)–Co–N(3) angle, on the other hand, assumes quite different values in the two compounds. The increase from 120.4 to 135.4° on going from $Co(Et_4dien)Cl_2$ to $Co(Me_5dien)Cl_2$ may be ascribed to the pressures exerted both on the central part of the ligand molecule, through the Cl(2)···C(5) contact, and on the two ends, through the other chlorine–methyl carbon contacts.

Distances and angles in the rest of the molecule do not differ by more than 3σ from the expected values, with the exception of the Co–N(2)–C(5) angle considered before. The few significant differences which are found between the two crystallographically independent molecules may be related to their different environments in the crystal. These differences involve mainly the coordination polyhedron and reach a maximum (6σ) in the Cl(2)–Co–N(1) angle. There are only two intermolecular contacts below 3.60 Å: a 3.53-Å contact between atoms Cl(2)′ (x, y, z) and C(2) $(x + 1, {}^1/_2 - y, {}^1/_2 + z)$ and a 3.58-Å contact between atoms C(2)′ (x, y, z) and C(7) $(\bar{x}, {}^1/_2 + y, {}^1/_2 - z)$.

The molecule of $Co(Me_5dien)Cl_2$ is approximately symmetrical with respect to a plane passing through the atoms Co, Cl(1), Cl(2), and N(2) (Table V). This pseudosymmetry is not present in the complex $Co(Et_4dien)Cl_2$, where the ligand molecule assumes a different conformation.

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The Crystal and Molecular Structure of N-Methyl-1,4-diazabicyclo[2.2.2]octonium Trichloroaquonickelate(II). A High-Spin Five-Coordinate Complex of Nickel(II) with Monodentate Ligands[1]

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N-Methyl-1,4-diazabicyclo[2.2.2]octonium trichloroaquonickelate(II), $C_7H_{15}N_2(H_2O)NiCl_3$, has been characterized by a three-dimensional X-ray diffractometer study. Refinement was carried out using full-matrix least-squares techniques on 1246 observed reflections to a final R value of 7.2%. The molecule crystallizes in the monoclinic space group $P2_1/m$ with unit cell dimensions $a = 8.173\ (4)$, $b = 9.393\ (5)$, $c = 7.769\ (4)$ Å; $\beta = 96°\ 40\ (2)'$; $Z = 2$; $\rho_{calcd} = 1.74$, $\rho_{obsd} = 1.73$ g/cm^3. The complex is monomeric with the N-methyl-1,4-diazabicyclo[2.2.2]octonium ion, $N(CH_2CH_2)_3N^+CH_3$, coordinated to the nickel atom through the unquaternized nitrogen. The resulting zwitterion has crystallographic symmetry m-C_s and is best described as a distorted trigonal bipyramid with equatorial chlorine atoms. Distortions are observed in the form of nonequivalent Ni–Cl bond lengths (one of 2.282 ± 0.002 Å and two of 2.339 ± 0.002 Å) and an axial N–Ni–O bond angle of 171°. These result chiefly from steric repulsions between the chlorine atoms and the cation ligand (causing all N–Ni–Cl bond angles to be greater than 90°) combined with intermolecular hydrogen bonding. The observed crystal stability is attributed to the presence of infinite chains formed by the latter interaction.

Introduction

Structure and bonding in halogen complexes of first-row transition metals have been subjects of interest in our laboratory for some time.[2–4] More recently, these interests have included complex stabilization by cation size and hydrogen-bonding effects.

N-Methyl-1,4-diazabicyclo[2.2.2]octonium trichloroaquonickelate(II) first attracted our interest for several reasons. The magnetic moment of 3.7 BM and the room-temperature diffuse reflectance spectrum were inconsistent with octahedral or tetrahedral coordination and appeared to be best explained by a high-spin five-coordinate geometry.[5] This was consistent with the empirical formula if one assumed that the cation, $N(CH_2CH_2)_3N^+CH_3$, also functioned as a monodentate ligand. With this in mind, a structural investigation was undertaken to confirm the five-coordinate geometry, to investigate the source of stabilization in detail, and possibly to aid in the interpretation of the observed spectroscopic and magnetic data.

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(2) (a) G. Stucky, S. D'Agostino, and G. McPherson, *J. Am. Chem. Soc.*, **88**, 4828 (1966); (b) G. Stucky, J. Folkers, and T. Kistenmacher, *Acta Cryst.*, **23**, 1064 (1967).

(3) G. Stucky, *ibid.*, **24B**, 330 (1968).

(4) T. Kistenmacher and G. Stucky, *Inorg. Chem.*, **7**, 2150 (1968).

(5) V. L. Goedken, J. V. Quagliano, and L. M. Vallarino, *ibid.*, **8**, 2331 (1969).