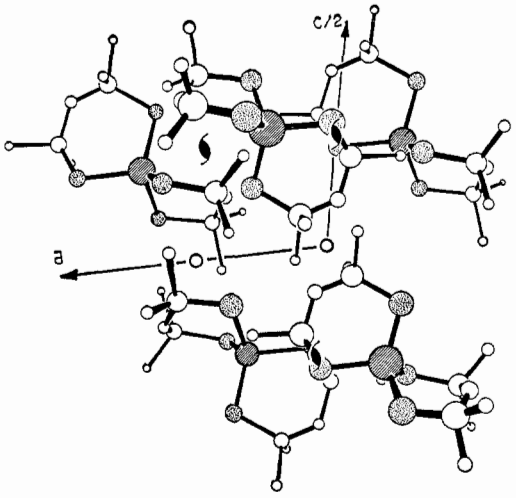

Figure 2.—Packing of $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$ molecules in the unit cell.

the energetically unfavorable boat conformation. In particular, we suspect that there are interactions between hydrogen atoms associated with the CH_3(axial) $\cdots$ CH_3(axial) contact, C(6)$\cdots$C(8) = 3.629 (13) Å (see Figure 1). [The CH_3(eq)$\cdots$$CH_3$(eq) contact, C(5)$\cdots$C(7), is 5.192 (14) Å.]

All other features of the structure of $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$ closely resemble those found in the analogous Ni(II) species.[3,4]

In summary, $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$ is the first confirmed example of a simple tetrahedral complex with an FeS_4 core. There is no ready explanation as to why the Fe(II) center has a tetrahedral (rather than square planar) coordination sphere, except that it may be noted that an S–Fe–S angle of 109° 28′ affords a more strain-free ligand geometry than would the square-planar angle of 90°.

The Crystal Structure

No intermolecular contacts of less than 3.5 Å were found. [This does not, however, include those involving hydrogen atoms, which were not detected in this analysis.] It is, nevertheless, clear that the crystal consists of independent molecular units of $[SP(CH_3)_2NP(CH_3)_2S]_2Fe^{II}$, held apart by normal van der Waals forces. The packing of molecules within the unit cell is illustrated in Figure 2.

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CONTRIBUTION FROM THE RESEARCH SCHOOL OF CHEMISTRY, AUSTRALIAN NATIONAL UNIVERSITY, CANBERRA, AUSTRALIA

The Crystal and Molecular Structure of Racemic (4-(2-Aminoethyl)-1,4,7,10-tetraazadecane)azidocobalt(III) Nitrate Hydrate

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The crystal and molecular structure of racemic (4-(2-aminoethyl)-1,4,7,10-tetraazadecane)azidocobalt(III) nitrate hydrate, *sym*-$[Co(trenen)N_3](NO_3)_2 \cdot H_2O$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in space group $P2_1/c$ (C_{2h}^5; no. 14), with a = 8.32 (1) Å, b = 7.64 (1) Å, c = 27.69 (3) Å, β = 96.3 (3)°, and Z = 4. Measured and calculated densities are 1.66 (2) and 1.64 (1) g cm^{-3}. Full-matrix least-squares techniques were used to refine the structure to a final residual R = 0.068 for 2030 independent nonzero reflections. The crystal is composed of *sym*-$Co(trenen)N_3^{2+}$ cations, NO_3^- anions, and water molecules which are held together by electrostatic forces and hydrogen bonds. The coordination at the metal ion is octahedral with the polyamine ligand coordinated quinquedentate and the azide ion occupying the remaining coordination site. The bifurcated structure of the ligand, trenen, and the mode of coordination have been determined. Ligand chelate ring conformations and the bonding requirements of the azide ion are discussed. Also the relationship between the structure of *sym*-$Co(trenen)N_3^{2+}$ and the base hydrolysis studies of the related chloro complex are discussed.

Introduction

As part of a general study on the stereochemistry and mechanisms of hydrolysis of complexes of the type CoN_5X^{2+} (where N_5 is a multidentate amine, a monodentate amine, ammonia, or a combination, and X is an acido group), four $Co(tetraen)X^{2+}$ (tetraen = tetraethylenepentamine) complexes were prepared and characterized.[1] The commercially available linear tetraen (Union Carbide) was known to contain a considerable percentage of some impurity, probably a branched-chain isomer. This posed the problem of deciding not only between topological isomers in the complexes but also between ligand isomers. In view of the very large number of isomeric possibilities, it was very difficult to make unequivocal structural assignments to the isolated complexes.

Detailed structural knowledge is essential to any comprehensive study of the mechanisms of hydrolysis of these compounds. Further, the conformations of the chelate rings in these types of complexes are of interest in determining the factors governing the geometries of multidentate amine complexes. Such information could be provided by a crystal structure analysis and

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(1) P. A. Marzilli, Ph.D. Thesis, Australian National University, 1968.

this paper describes the results of an X-ray structural analysis on a $Co(tetraen)N_3^{2+}$ complex. The azido complex is known to be structurally related to the chloro complex isolated as the first fraction from the reaction mixture. Therefore the results of this analysis will be relevant to the kinetic studies on the chloro complex. Also accurate structural data on coordinated azide is sparse and additional data might aid in defining the bonding requirements for coordinated azide ion. Suitable single crystals of the racemic complex were obtained as the dinitrate salt.

Experimental Section

Crystal Data.—*rac*-$[Co(tetraen)N_3](NO_3)_2 \cdot H_2O$ crystallized in well-formed air-stable orange crystals. The unit cell is monoclinic with $a = 8.32$ (1) Å, $b = 7.64$ (1) Å, $c = 27.69$ (3) Å, $\beta = 96.3$ (3)°, $V = 1749.6$ Å^3, $d_m = 1.66$ (2) g cm^{-3} (by flotation in bromoethane–ethanol), $Z = 4$, $d_x = 1.64$ (1) g cm^{-3} for $C_8H_{25}N_{10}O_7Co$ with FW 452.4, $\mu_{CuK\alpha} = 86.2$ cm^{-1}. From systematic absences of reflections ($h0l$ absent for $l = 2n + 1$, $0k0$ absent for $k = 2n + 1$) the space group was determined to be $P2_1/c$ (C_{2h}^5; no 14). Unit cell dimensions were calculated from θ measurements on high-angle reflections using an equiinclination diffractometer and Ni-filtered Cu Kα radiation [λ(Cu Kα_1) 1.5405 Å, λ(Cu Kα_2) 1.5443 Å].

X-Ray Data Collection and Reduction.—Two crystals of dimensions 0.10 × 0.05 × 0.04 mm and 0.07 × 0.20 × 0.04 mm (parallel to axes a, b, and c, respectively) were mounted about the a and b axes, respectively, for data collection. Data were collected on an automated Buerger–Supper equiinclination diffractometer using Ni-filtered Cu Kα radiation from a fully stabilized X-ray generator. The control program was an early version of that described by Freeman, *et al.*[2] The reflection indices hkl, setting angles ϕ (crystal) and γ (counter), and scan range ω were input from punched paper tape. The background and peak intensities B_1, P, B_2 were recorded under computer control, using a sequence of operations analogous to those previously described.[3]

The angle subtended at the crystal by the counter aperture was increased with increasing μ in the range 2° 50′–3° 50′. A constant scan of 3°/min was used and the scan range was generally 3°, being increased for very extended reflections. Attenuation of the X-ray beam was not necessary since the maximum observed count rate was within the linear range of the counter.

Reflection data were collected in the range $10° \leq \gamma \leq 140°$ for the zone $Hk0$ and levels hKl and $hK\bar{l}$ ($0 \leq K \leq 6$). The net count $I(hkl)$ for each reflection was calculated as $I(hkl) = P - (B_1 + B_2)$ where P is the spot count and B_1 and B_2 are the first and second background counts. A reflection was considered unobserved if $I(hkl) < 2(B_1 + B_2)^{1/2}$. Lorentz–polarization corrections were applied and estimated standard deviations were calculated by the method of Hoard and Jacobson,[4] using values of 0.02, 0.05, and 0 for K_T, K_B, and K_D, the estimated errors in peak count, background count, and correction for crystal decomposition, respectively. Absorption corrections were applied by the method of Coppens, Leiserowitz, and Rabinovich.[5] The grids used were 2 × 10 × 6 and 4 × 10 × 2 (parallel to a, b, and c) for the a- and b-axis crystals, respectively. Calculated transmission coefficients were in the ranges 0.71–0.77 and 0.55–0.72 for the a- and b-axis crystals, respectively. Scale factors between layers were calculated by a least-squares procedure[6] and indicated some decomposition of the b-axis crystal (maximum 10%). A total of 2739 independent reflections were obtained of which 709 were unobservably weak.

Solution and Refinement of the Structure.—The structure was solved using a sharpened Patterson synthesis and the usual Fourier analyses. One molecule of water of crystallization was located from a $(F_o - F_c)$ synthesis calculated in the final stages of solution of the structure. Full-matrix least-squares refinement was carried out minimizing the function $\Sigma w(|F_o| - s|F_c|)^2$ where $w = 1/\sigma^2(F)$ and s is the inverse of the scale factor applied to F_o. The unobserved reflection data were assigned zero weights. Initially convergence problems were encountered in the least-squares refinement which were attributed to an incorrect weighting scheme. These problems were resolved when unit weights were applied, and after two cycles were carried out varying an overall scale factor, atomic coordinates, and isotropic temperature factors, the residuals $R_1 = \Sigma\Delta/\Sigma|F_o|$ and $R_2 = [\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}$ were 0.150 and 0.174, respectively ($\Delta = ||F_o| - s|F_c||$).

An improved weighting scheme was obtained from an analysis of $\langle 1/\Delta^2 \rangle$ in ranges of $|F_o|$ and $(\sin\theta)/\lambda$. The $|F_o|$ dependence was fitted to a modified Cruickshank function[7] of the type $w = K/[1 - ((F_o - p_2)/p_1)^2]$. This type of analysis was repeated after each subsequent cycle and the parameters K, p_1, and p_2 were modified to fit the F_o dependence.

A $(F_o - F_c)$ synthesis after a further cycle of refinement in which anisotropic temperature factors were varied indicated significant electron density in the regions where hydrogen atoms of the ligand would be expected. The inclusion of ligand hydrogen atoms at calculated positions reduced R_1 from 0.089 to 0.085. Hydrogen atom positions were recalculated after each subsequent refinement cycle. The refinement converged (maximum parameter shift 0.3σ) after three more cycles to residuals $R_1 = 0.068$ and $R_2 = 0.072$. Final weighting parameters were $K = 0.312$, $p_1 = 17.6$, and $p_2 = 34.0$. A difference Fourier synthesis using the refined coordinates had no maxima greater than 0.4 e$^-$/Å^3 (except in the vicinity of the cobalt, maximum density 0.8 e$^-$/Å^3).

The scattering factor tables for Co^{3+}, O, N, and C were those listed by Cromer and Waber[8] and the hydrogen curve was taken from ref 9. Cobalt was treated as an anomalous scatterer using the $\Delta f'$ and $\Delta f''$ values given by Cromer.[10] Observed and calculated structure factors are listed in Table I. Final atomic positional and thermal parameters along with their estimated standard deviations are given in Table II. A perspective diagram of the complex cation showing atom numbering and ellipsoids of thermal motion is given in Figure 1.

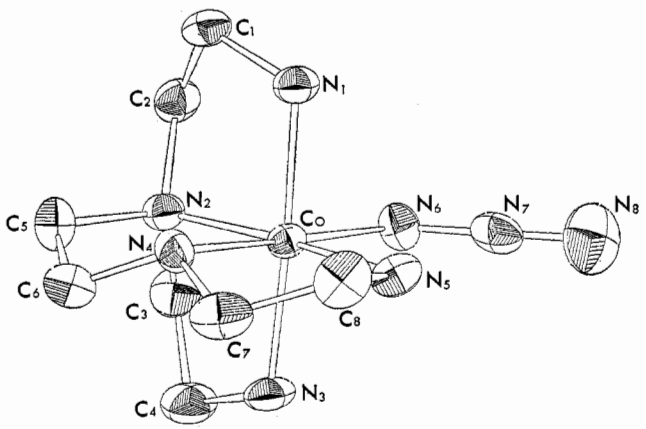

Figure 1.

Description of the Structure

Introduction.—The crystal structure consists of discrete complex cations and nitrate anions along with one molecule of water of crystallization per cation (Figure 2). Each complex cation is asymmetric; thus the centrosymmetric unit cell contains two pairs of enantiomers. The crystal lattice is held together by a combination of electrostatic forces and a complex hydrogen-bonding network.

Hydrogen Bonding and Nonbonded Contacts.—Hydrogen bond distances and angles, along with the identification of donor and acceptor atoms, are given

(2) H. C. Freeman, J. M. Guss, C. E. Nockolds, R. Page, and A. Webster, *Acta Crystallogr., Sect. A*, **26**,149 (1970).

(3) H. C. Freeman and I. E. Maxwell, *Inorg. Chem.*, **8**, 1293 (1969).

(4) L. C. Hoard and R. A. Jacobson, *J. Chem. Soc. A*, 1203 (1966).

(5) P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Crystallogr.*, **18**, 1035 (1965).

(6) (a) A. D. Rae, *ibid.*, **19**, 683 (1965); (b) A. D. Rae and A. B. Blake, *ibid.*, **20**, 586 (1966).

(7) J. S. Rollett and O. S. Mills in "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," R. Pepinsky, Ed., Pergamon Press, Oxford, 1961, p 117.

(8) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(9) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, p 202.

(10) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

Table I

Observed and Calculated Structure Amplitudes (in electrons ×10) for $[Co(trenen)N_3](NO_3)_2 \cdot H_2O$

K	L	Fo	Fc
*** H = 0 ***			
2	0	421	365
4	0	188	181
6	0	135	124
8	0	121	140
2	1	532	500
4	1	694	702
5	1	189	173
6	1	176	72
9	1	225	221
1	2	735	671
2	2	531	545
3	2	575	550
4	2	154	139
5	2	101	69
8	2	105	142
9	2	225	232
2	3	1313	1264
3	3	645	608
4	3	193	191
5	3	275	306
6	3	110	83
7	3	201	218
0	4	832	965
1	4	374	381
2	4	167	175
3	4	124	116
4	4	617	616
5	4	62	68
7	4	191	168
8	4	160	192
1	5	193	140
2	5	264	240
3	5	643	651
4	5	634	680
5	5	182	196
0	6	201	146
1	6	1186	1157
2	6	624	640
3	6	475	464
4	6	115	138
5	6	422	451
6	6	87	109
7	6	121	149
8	6	146	89
9	6	126	140
1	7	544	556
2	7	553	565
3	7	57	31
4	7	144	135
5	7	123	141
6	7	165	135
7	7	317	321
0	8	1125	1107
1	8	780	793
2	8	251	248
3	8	568	577
4	8	512	537
5	8	307	317
6	8	130	164
8	8	117	166
1	9	1025	1050
2	9	486	480
3	9	384	382
4	9	605	611
5	9	237	246
6	9	166	155
8	9	225	239
0	10	1292	1357
1	10	1082	1074
2	10	177	191
3	10	459	456
4	10	95	68
5	10	141	149
6	10	173	132
1	11	831	809
2	11	275	271
3	11	276	267
4	11	158	164
5	11	252	252
7	11	225	224
0	12	558	571
1	12	522	512
2	12	184	153
3	12	305	328
4	12	228	218
5	12	174	178
1	13	331	366
2	13	525	544
3	13	384	359
4	13	204	221
5	13	106	91
7	13	160	191
8	13	138	123
0	14	712	715
1	14	272	295
2	14	517	550
3	14	120	142
5	14	203	215
6	14	205	199
1	15	733	724
2	15	541	552
3	15	472	465
4	15	386	355
5	15	282	266
6	15	125	84
0	16	274	277
1	16	455	451
2	16	83	56
3	16	475	494
4	16	158	133
1	17	438	434
2	17	362	351
3	17	115	52
5	17	147	172
7	17	110	75
0	18	227	220
1	18	253	239
2	18	365	365
3	18	216	205
4	18	177	149
5	18	228	205
6	18	163	182
7	18	185	185
2	19	326	332
3	19	152	67
4	19	265	283
7	19	157	165
0	20	150	160
1	20	468	482
2	20	243	249
3	20	247	266
5	20	165	148
6	20	167	166
1	21	367	377
2	21	318	311
3	21	128	121
5	21	121	139
7	21	143	132
0	22	326	320
2	22	131	118
4	22	124	131
5	22	103	117
6	22	124	133
2	23	436	429
4	23	105	99
0	24	296	319
1	24	276	277
2	24	268	283
3	24	343	325
6	24	225	232
1	25	268	285
3	25	123	104
5	25	275	272
0	26	122	121
1	26	255	235
3	26	235	249
4	26	95	90
5	26	207	207
1	27	252	252
2	27	205	226
3	27	108	37
4	27	157	148
5	27	120	84
0	28	173	175
1	28	143	155
2	28	251	263
4	28	128	115
1	29	130	131
2	29	161	147
4	29	140	145
0	30	234	227
1	30	106	67
2	30	91	18
3	30	223	208
1	31	106	92
2	31	155	158
0	32	260	265
1	32	74	35
2	32	151	153
*** H = 1 ***			
1	0	857	785
2	0	557	525
3	0	305	294
4	0	62	29
5	0	277	275
1	-1	345	295
2	1	555	520
2	-1	452	412
3	1	167	170
3	-1	312	320
4	1	295	285
4	-1	482	480
5	1	395	358
6	1	80	85
0	2	1795	1768
0	-2	1155	1522
1	2	515	514
1	-2	47	34
3	2	1287	1174
3	-2	374	367
5	-2	71	122
6	-2	295	274
1	3	858	816
1	-3	496	441
2	3	370	345
2	-3	91	96
3	3	532	853
3	-3	105	107
5	-3	132	136
6	3	76	64
6	-3	62	30
0	4	834	812
0	-4	1005	986
1	4	450	379
1	-4	694	636
2	4	359	363
2	-4	358	428
3	4	810	793
4	-4	132	155
5	-4	408	448
6	4	261	285
6	-4	81	85
1	5	663	625
1	-5	556	571
2	-5	708	708
3	-5	98	81
5	5	78	112
5	-5	266	280
6	5	91	56
0	6	463	386
0	-6	1407	1430
1	6	870	860
1	-6	109	113
2	6	344	323
3	6	104	110
5	6	194	155
5	-6	372	399
6	6	91	124
6	-6	155	195
1	7	623	550
1	-7	148	147
2	7	573	566
2	-7	123	118
3	7	434	416
3	-7	65	9
5	7	125	156
6	7	112	116
6	-7	76	88
0	8	698	723
0	-8	891	885
1	8	830	817
1	-8	346	356
2	8	356	355
2	-8	527	533
3	8	282	266
5	-8	206	215
6	8	208	221
6	-8	84	68
1	9	126	124
1	-9	767	743
2	9	225	208
2	-9	105	130
3	9	261	253
3	-9	165	128
4	9	86	113
5	-9	457	508
6	-9	151	145
0	10	805	828
0	-10	1344	1441
1	10	270	272
1	-10	285	281
2	10	464	495
2	-10	180	189
3	-10	423	439
4	10	151	182
4	-10	105	137
5	10	191	205
5	-10	297	321
6	10	342	355
6	-10	189	180
1	11	413	439
1	-11	287	267
2	11	771	785
2	-11	469	503
3	-11	197	174
4	11	123	68
5	-11	175	188
6	-11	126	129
0	12	1025	1078
0	-12	1301	1356
1	12	235	237
1	-12	197	232
2	12	424	434
2	-12	556	584
3	12	235	244
3	-12	310	309
4	12	244	278
5	12	107	91
5	-12	133	162
6	12	372	381
6	-12	273	260
1	13	494	504
1	-13	556	580
2	13	315	332
3	13	260	255
3	-13	338	328
4	13	343	379
4	-13	353	373
5	13	263	279
5	-13	403	410
0	14	322	317
0	-14	262	252
1	14	545	545
2	14	261	269
2	-14	546	556
3	14	671	701
3	-14	335	352
4	14	277	270
4	-14	246	256
5	-14	220	264
1	15	598	612
1	-15	604	607
2	15	262	270
2	-15	173	202
3	15	150	135
3	-15	227	232
4	15	209	215
4	-15	255	258
5	15	395	405
6	15	145	124
0	16	421	440
0	-16	514	539
1	16	311	331
1	-16	351	383
2	16	358	377
2	-16	254	258
3	16	143	120
3	-16	105	85
4	-16	111	93
6	16	124	135
1	17	187	163
1	-17	787	786
2	17	643	656
2	-17	318	312
3	17	373	370
4	17	224	227
4	-17	103	131
5	17	132	123
5	-17	168	188
6	17	118	112
6	-17	102	25
0	18	141	138
0	-18	173	180
1	18	337	327
1	-18	100	64
2	18	165	169
2	-18	187	194
3	18	178	192
3	-18	462	440
4	18	331	352
4	-18	196	209
5	-18	191	195
6	18	172	201
1	19	119	125
1	-19	432	433
2	-19	287	285
4	19	138	185
4	-19	256	253
5	19	233	237
5	-19	112	96
6	19	117	122
0	20	232	224
0	-20	268	286
1	20	134	142
1	-20	85	27
2	20	225	218
2	-20	102	91
3	20	116	128
3	-20	244	247
6	20	207	193
6	-20	412	386
2	21	214	170
2	-21	356	340
3	21	236	254
4	21	260	262
4	-21	301	296
5	-21	236	238
6	21	95	56
0	22	415	420
1	22	126	98
1	-22	188	207
2	22	255	270
2	-22	155	143
3	22	303	297
3	-22	495	469
4	22	114	159
4	-22	185	171
5	-22	122	128
6	22	195	214
6	-22	171	135
1	23	392	389
1	-23	108	99
2	23	120	129
2	-23	275	258
3	23	155	147
5	23	245	238
5	-23	248	239
0	24	263	264
0	-24	158	145
1	24	123	89
1	-24	103	71
2	-24	135	91
3	24	324	313
3	-24	185	187
4	24	180	165
4	-24	162	154
5	24	133	115
5	-24	300	283
6	-24	236	204
1	25	181	174
1	-25	145	174
2	25	133	156
2	-25	300	268
3	25	105	99
3	-25	121	75
4	25	144	152
4	-25	183	181
0	26	290	294
0	-26	316	312
1	26	101	45
1	-26	312	311
2	26	168	175
2	-26	184	149
3	-26	144	119
1	27	262	258
1	-27	298	278
2	27	235	237
2	-27	94	57
4	27	114	65
5	-27	132	130
0	28	207	211
0	-28	123	165
1	28	215	212
1	-28	122	91
3	28	333	312
3	-28	175	180
4	-28	84	109
1	29	202	198
1	-29	100	86
2	29	134	157
2	-29	297	308
4	-29	100	57
0	30	260	277
0	-30	252	247
1	30	98	75
1	-30	98	65
2	30	188	184
2	-30	195	195
3	-30	100	104
1	31	84	37
1	-31	201	171
2	31	276	261
2	-31	155	157
3	-31	142	148
1	32	72	40
1	-32	157	141
*** H = 2 ***			
0	0	706	616
1	0	618	571
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Table I (*Continued*)

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6	-4	142	53
6	4	268	249
6	-4	142	110
1	5	114	92
2	5	294	311
2	-5	318	325
3	5	175	180
4	5	135	149
4	-5	995	952
5	5	227	219
5	-5	114	52
0	6	103	127
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1	6	347	331
1	-6	133	146
2	6	192	212
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2	7	305	317
4	7	210	196
5	7	131	87
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6	7	125	135
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0	-8	174	185
2	8	308	303
2	-8	124	86
3	8	428	424
3	-8	356	340
4	-8	226	214
5	8	113	62
5	-8	213	211
6	8	234	234
6	-8	332	91
1	-9	192	172
2	9	670	662
2	-9	325	330
4	9	210	156
4	-9	360	359
5	-9	190	207
6	-9	97	129
0	10	413	640
0	-10	240	222
1	10	188	180
1	-10	258	289
2	10	107	151
2	-10	136	154
3	10	368	357
3	-10	135	179
4	-10	190	156

K	L	Fo	Fc
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6	-10	275	266
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1	-11	600	611
2	11	115	76
2	-11	107	104
3	-11	110	50
4	-11	272	287
5	-11	271	280
0	-12	126	144
1	12	293	266
1	-12	184	174
2	12	256	268
2	-12	147	149
3	12	190	224
3	-12	296	302
4	-12	256	255
5	12	131	90
5	-12	263	258
6	12	204	156
1	13	178	177
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3	13	145	150
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0	14	365	359
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1	14	115	112
1	-14	125	127
2	14	161	192
2	-14	285	310
3	14	264	288
4	14	113	151
4	-14	174	233
6	14	194	189
6	-14	163	161
1	15	314	340
1	-15	375	363
2	15	272	271
2	-15	262	262
3	-15	178	169
4	15	232	214
4	-15	143	157
5	15	211	203
5	-15	227	227
0	16	104	49
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1	16	201	190
1	-16	237	231
2	16	166	158
3	16	337	345
3	-16	397	389
5	16	164	165
5	-16	175	174
1	17	175	182
1	-17	303	328
2	17	207	201
4	-17	183	157
5	17	195	204
5	-17	261	253
6	-17	115	107
0	18	225	234
0	-18	318	321
1	-18	144	142
2	-18	418	419
3	18	127	100
3	-18	278	263
4	18	133	90
6	-18	222	184
1	19	220	218
2	19	258	246
2	-19	314	309
4	19	114	85
4	-19	350	339
5	19	80	44
0	-20	380	385
1	20	253	261
2	-20	149	156
3	20	158	159
3	-20	196	179
5	-20	174	140

K	L	Fo	Fc
1	21	228	233
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2	-21	100	71
5	-21	125	107
0	22	255	266
0	-22	125	148
1	22	92	104
2	22	177	147
2	-22	123	124
3	-22	118	106
4	22	118	85
4	-22	125	105
2	23	261	244
2	-23	143	152
3	-23	97	111
4	-23	256	218
0	24	239	245
0	-24	151	155
1	24	91	66
1	-24	112	66
2	24	122	107
3	24	97	107
3	-24	347	330
1	25	274	256
1	-25	285	267
2	-25	116	66
4	-25	96	77
0	26	226	238
0	-26	140	146
1	26	106	113
1	-26	275	247
2	-26	103	78
3	-26	201	207
4	-26	140	110
1	-27	152	176
2	-27	211	205
0	-28	203	156
2	-28	107	121
3	-28	98	85
2	-29	145	139
0	-30	85	82
1	-30	98	64
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2	0	165	184
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6	0	135	57
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2	1	247	255
2	-1	413	423
3	1	245	233
3	-1	157	141
4	1	111	57
4	-1	219	213
5	1	197	176
5	-1	217	213
0	2	153	121
0	-2	360	367
2	2	288	288
2	-2	207	245
3	2	300	298
4	2	111	55
4	-2	188	178
5	2	132	121
6	2	278	284
6	-2	358	350
1	3	272	266
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2	3	580	582
2	-3	608	621
3	3	155	181
3	-3	262	246
4	3	127	55
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1	-4	140	171
3	4	360	356
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4	4	197	173

K	L	Fo	Fc
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6	4	263	240
6	-4	229	224
1	5	111	118
1	-5	251	251
2	5	200	180
4	5	127	83
4	-5	109	143
5	5	208	173
5	-5	325	331
0	6	215	236
0	-6	156	170
1	6	307	301
1	-6	134	170
2	6	125	101
2	-6	102	100
3	6	212	223
3	-6	236	227
4	-6	109	114
5	6	143	138
6	6	291	290
6	-6	183	177
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2	8	166	173
3	8	195	193
3	-8	184	198
4	8	144	137
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6	-8	97	107
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2	10	338	362
2	-10	106	86
3	10	143	155
3	-10	244	249
4	10	173	163
4	-10	184	158
6	10	161	148
6	-10	174	145
1	11	158	171
2	11	382	376
2	-11	192	206
3	11	177	186
3	-11	232	230
4	11	141	170
4	-11	307	308
6	11	103	52
6	-11	116	123
0	12	501	510
0	-12	232	245
2	12	305	306
2	-12	185	174
3	-12	261	280
4	-12	185	180
5	12	141	151
6	12	294	265
6	-12	312	290
1	13	273	269
1	-13	401	395
2	13	298	282
4	13	158	141
4	-13	154	114
5	13	165	123
5	-13	264	268
6	-13	95	65
0	14	109	91

K	L	Fo	Fc
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1	-14	205	223
3	14	210	230
3	-14	274	275
4	14	115	87
4	-14	113	124
5	-14	145	165
1	-15	330	327
2	-15	285	284
3	-15	124	157
4	-15	121	134
5	15	254	246
5	-15	181	205
0	16	166	166
0	-16	412	437
1	16	151	174
1	-16	150	155
2	-16	189	181
3	-16	180	193
4	16	148	158
4	-16	178	179
5	-16	98	35
6	-16	221	211
2	17	188	214
2	-17	111	94
3	-17	216	209
4	17	116	58
4	-17	256	250
5	-17	206	172
0	-18	227	245
1	18	154	144
1	-18	121	73
3	18	182	178
3	-18	236	242
5	-18	105	158
1	19	182	165
1	-19	128	115
3	-19	146	105
4	19	152	149
4	-19	114	111
5	-19	93	112
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1	20	151	136
4	-20	115	59
1	-21	233	243
2	21	146	152
2	-21	138	139
3	21	123	133
4	-21	286	296
0	22	109	80
0	-22	122	135
3	-22	230	224
1	23	159	175
1	-23	177	172
0	24	252	257
2	-24	145	122
3	-24	141	150
2	-25	148	127
3	-25	111	73
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1	-27	134	152
2	-27	103	68
0	-28	125	106
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3	1	154	136
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0	2	335	330
0	-2	223	243
1	2	105	94
1	-2	251	237
2	2	278	285
3	2	213	202

K	L	Fo	Fc
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6	2	230	217
6	-2	119	89
1	3	105	105
1	-3	250	258
2	-3	267	273
5	3	262	303
5	-3	180	185
0	4	234	254
1	-4	152	187
1	4	127	126
1	-4	144	153
2	-4	314	322
3	4	121	137
4	4	110	109
5	-4	185	179
6	4	127	137
6	-4	297	279
1	5	131	119
1	-5	297	295
2	-5	238	282
3	5	155	102
3	-5	166	145
5	5	144	151
5	-5	157	147
0	6	158	156
1	6	108	120
2	6	160	183
3	6	108	106
3	-6	278	274
5	6	121	149
5	-6	197	157
1	7	290	289
1	-7	223	223
3	-7	135	138
4	-7	162	138
5	7	228	228
5	-7	130	155
0	8	216	228
0	-8	278	289
1	-8	335	325
2	-8	210	224
3	8	195	233
3	-8	123	71
5	8	189	186
6	-8	291	274
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1	-9	267	279
2	9	170	160
2	-9	362	360
3	9	280	276
4	9	142	135
4	-9	115	121
1	10	210	180
0	-10	145	176
1	10	176	134
2	10	201	184
2	-10	133	124
3	-10	270	257
4	10	148	154
4	-10	148	114
5	-10	101	128
6	-10	109	132
1	11	175	151
1	-11	136	102
2	11	190	152
3	11	140	160
4	11	121	133
4	-11	144	155
5	11	142	150
5	-11	258	253
0	12	173	181
0	-12	203	211
1	12	161	123
1	-12	351	340
3	12	211	218
3	-12	197	169
4	-12	144	123
1	13	148	123
2	13	95	45
2	-13	377	375
4	13	183	175
1	-13	253	241

K	L	Fo	Fc
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2	14	143	164
3	-14	184	201
4	14	93	51
4	-14	130	119
5	14	168	164
1	15	96	107
1	-15	151	155
2	15	237	224
4	15	193	178
5	-15	138	162
0	16	110	117
1	16	112	107
2	16	106	126
3	16	218	211
3	-16	231	211
5	-16	91	43
1	17	103	116
2	17	105	72
2	-17	108	104
4	-17	232	220
5	-17	156	136
0	18	103	70
0	-18	416	413
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1	-18	210	203
2	-18	133	144
3	18	121	101
3	-18	97	104
4	-18	95	82
1	19	78	22
1	-19	242	259
2	19	82	80
2	-19	137	144
4	-19	81	105
0	20	89	64
0	-20	102	85
1	-20	181	169
2	-20	105	93
3	-20	140	159
4	-20	75	99
1	-21	91	74
2	-21	98	58
3	-21	86	64
0	-22	218	242
1	-22	87	45
3	-22	81	63
1	-23	153	160
2	-23	115	112
0	-24	118	134
2	-24	125	116
1	-25	222	206
0	-26	168	188
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3	0	204	182
1	1	156	166
2	-1	285	312
3	-1	117	150
4	-1	201	190
5	1	260	267
0	2	154	119
0	-2	423	430
1	-2	235	222
2	-2	156	181
3	2	162	168
5	-2	100	114
1	-3	435	432
2	3	236	234
2	-3	102	52
3	-3	151	153
4	3	255	251
4	-3	101	86
5	-3	155	113
0	4	346	368
3	-4	263	286
5	-4	92	65
1	5	228	225
1	-5	278	268
2	5	105	151
2	-5	185	156
4	5	128	119

K	L	Fo	Fc
4	-5	122	149
0	6	111	51
1	-6	110	99
2	6	206	204
2	-6	186	192
3	6	255	256
4	6	139	150
4	-6	122	105
1	7	163	163
1	-7	196	165
2	-7	180	165
3	7	135	151
4	7	158	149
4	-7	85	72
5	-7	161	178
0	8	180	176
1	-8	168	152
2	-8	143	139
3	-8	166	177
4	-8	125	105
5	-8	168	173
1	9	147	161
2	9	205	182
2	-9	213	227
4	-9	103	152
5	-9	144	160
0	10	147	147
2	-10	364	350
3	10	293	285
3	-10	151	174
4	10	113	90
4	-10	140	131
1	11	141	135
1	-11	188	147
2	11	172	138
2	-11	258	263
4	-11	185	183
0	12	208	245
0	-12	157	171
1	-12	125	78
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0	14	207	194
0	-14	184	183
1	-14	245	221
2	-14	95	86
3	-14	161	161
1	15	182	194
1	-15	107	126
2	-15	265	270
4	-15	96	108
0	-16	107	96
2	-16	132	135
3	-16	197	209
1	-17	226	234
0	-18	88	105
1	-18	201	264
2	-18	185	156
3	-18	155	177
1	-19	148	82
2	-19	178	173
0	-20	296	317
2	-20	181	161
1	-21	165	181
2	-21	153	129
1	-22	112	103
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1	-1	238	256
2	1	152	223
0	2	355	350
0	-2	163	169
1	-2	112	101
3	-2	144	170
1	3	156	223
2	3	132	182
2	-3	233	248
0	-4	147	143
1	-4	103	127

K	L	Fo	Fc
3	4	120	151
3	-4	162	173
1	-5	240	242
2	5	133	155
0	6	170	186
0	-6	93	71
1	-6	147	158
2	6	109	94
3	-6	267	253
1	-7	220	224
2	7	135	133
2	-7	273	268
0	8	141	107
0	-8	360	392
1	8	128	111
1	-8	154	155
1	9	200	188
1	-9	133	122
2	-9	125	112
0	10	240	257
0	-10	95	26
3	-10	192	188
1	-11	92	94
3	-11	130	86
0	-12	272	298
2	-12	142	158
1	-13	221	155
2	-13	181	175
1	-14	166	161
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2	-15	102	88
0	-16	135	151
•			

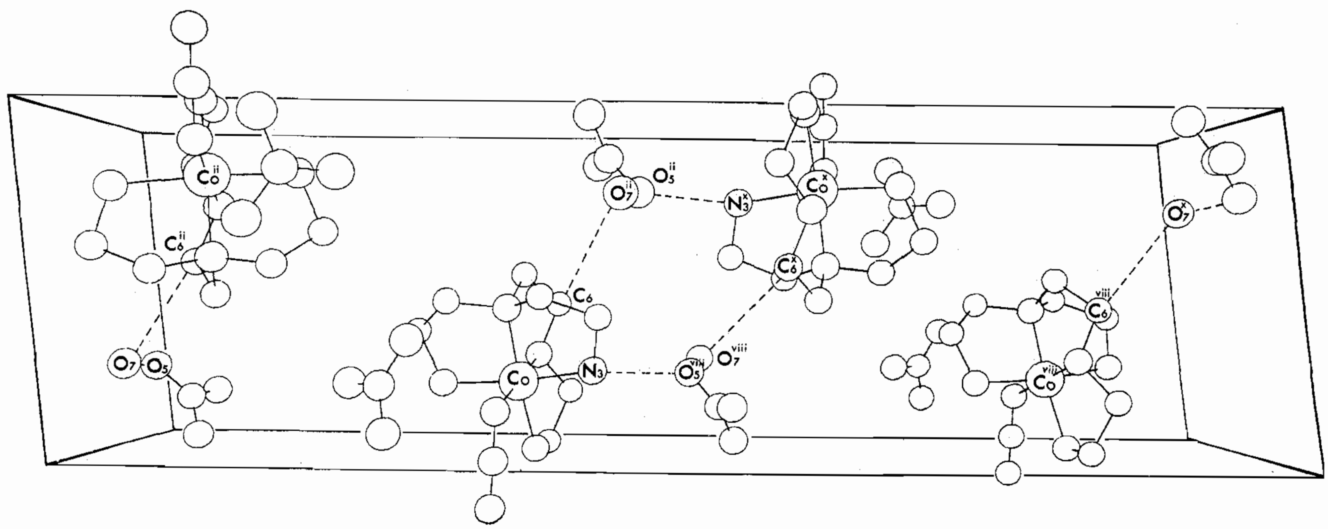

Figure 2.

in Table III. The nitrogen atoms of each cation make seven hydrogen bonds with the oxygen atoms of four neighboring nitrate anions. Each nitrate ion hydrogen bonds to two adjacent complex cations and each water molecule H bonds to two adjacent nitrate groups. The H-bonding scheme is complex and is shown partly in Figure 2.

Closest nonbonded contacts occur between cations and nitrate anions and are as follows: C(6)–O(7)^{iii}, 3.16 Å; N(7)$\cdots$O(6)^{vi}, 3.19 Å; N(7)$\cdots$O(3)^{iv}, 3.20 Å;

TABLE II
FRACTIONAL ATOMIC POSITIONAL PARAMETERS[a-c] AND ANISOTROPIC TEMPERATURE FACTORS[d] FOR $[Co(trenen)N_3](NO_3)_2 \cdot H_2O$

Atom	10^4x	10^4y	10^4z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$	Atom	10^4x	10^4y	10^4z
Co	2044(1)	4182(2)	3589(1)	70(1)	80(2)	6(1)	-5(2)	4(1)	-2(1)	H(1)	1583	2601	2825
O(1)	2193(7)	8070(7)	2309(2)	221(11)	111(11)	10(1)	-2(9)	2(2)	-11(2)	H(2)	1202	4564	2725
O(2)	3473(6)	9567(7)	2895(2)	108(7)	144(12)	11(1)	-23(7)	3(2)	-9(2)	H(3)	4197	2761	2723
O(3)	961(6)	10112(7)	2667(2)	119(8)	125(12)	19(1)	29(8)	4(2)	-9(3)	H(4)	3422	4509	2347
O(4)	1358(7)	69(9)	480(2)	190(11)	147(14)	15(1)	36(9)	10(2)	17(3)	H(5)	5770	5302	3001
O(5)	2286(7)	2348(9)	143(2)	180(10)	234(15)	13(1)	-26(10)	21(2)	8(3)	H(6)	4018	6621	2992
O(6)	90(7)	2539(8)	481(2)	174(10)	199(14)	17(1)	38(10)	19(2)	-2(3)	H(7)	5965	6515	3962
O(7)	2543(9)	6162(10)	265(3)	284(15)	237(19)	25(1)	11(13)	-17(4)	-2(4)	H(8)	4056	7442	3763
N(1)	1930(6)	3767(8)	2889(2)	90(8)	135(14)	7(1)	-3(8)	5(2)	-2(2)	H(9)	4893	4842	4575
N(2)	4318(6)	4776(8)	3566(2)	86(8)	103(13)	7(1)	6(7)	5(2)	-2(2)	H(10)	3987	6930	4607
N(3)	2426(7)	4973(8)	4277(2)	116(9)	149(13)	6(1)	-17(9)	7(2)	-8(2)	H(11)	2365	3983	4484
N(4)	2763(6)	1786(8)	3729(2)	91(8)	125(13)	8(1)	16(8)	3(2)	6(3)	H(12)	1641	5803	4338
N(5)	-140(6)	3291(8)	3649(2)	103(9)	116(14)	10(1)	-21(9)	9(2)	-6(3)	H(13)	5753	2626	3386
N(6)	1301(6)	6568(8)	3433(2)	80(9)	127(14)	9(1)	3(8)	-1(2)	2(2)	H(14)	6389	3620	3952
N(7)	-135(7)	6864(8)	3382(2)	131(12)	95(13)	8(1)	-8(9)	1(2)	6(2)	H(15)	4969	539	3942
N(8)	-1484(8)	7235(10)	3327(3)	107(11)	219(20)	23(1)	-48(12)	1(3)	-9(4)	H(16)	4402	2155	4349
N(9)	2206(7)	9234(8)	2620(2)	137(10)	83(12)	8(1)	-20(10)	2(2)	3(3)	H(17)	2812	1277	3442
N(10)	1257(7)	1638(10)	370(2)	136(11)	170(17)	8(1)	2(11)	7(2)	-1(3)	H(18)	1701	-536	3956
C(1)	3554(8)	4007(10)	2716(2)	111(10)	115(16)	7(1)	-6(11)	11(2)	1(3)	H(19)	1621	1261	4356
C(2)	4496(8)	5306(10)	3057(2)	97(10)	134(17)	9(1)	-5(10)	11(2)	2(3)	H(20)	-324	739	3368
C(3)	4679(8)	6264(10)	3908(3)	108(11)	109(17)	11(1)	-14(10)	1(3)	-12(3)	H(21)	-1074	1005	3938
C(4)	4068(8)	5780(12)	4384(2)	124(11)	192(19)	8(1)	-21(13)	1(2)	-15(4)	H(22)	-832	3574	3366
C(5)	5345(8)	3193(11)	3711(3)	92(11)	141(17)	12(1)	35(11)	4(3)	5(3)	H(23)	-540	3827	3925
C(6)	4403(9)	1819(11)	3971(3)	131(12)	151(18)	9(1)	12(12)	-2(3)	4(3)				
C(7)	1524(9)	853(11)	3978(2)	169(13)	96(16)	11(1)	-8(13)	7(3)	6(3)				
C(8)	-117(9)	1375(10)	3723(3)	141(13)	100(18)	14(1)	-37(11)	11(3)	2(3)				

[a] Numbers in parentheses are estimated standard deviations right-adjusted to the least significant digit of the preceding number. [b] Hydrogen atom positions were calculated as follows: tetrahedral primary N, $d_{N-H} = 0.95$ Å; tetrahedral secondary N, $d_{N-H} = 0.89$ Å; methylene C, $d_{C-H} = 1.084$ Å. [c] Hydrogen atoms are numbered sequentially around the chelate rings from atom N(1) to atom N(5). [d] The form of the anisotropic temperature parameter T is $T = \exp\{-[h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2\ kl\beta_{23}]\}$.

N(8)···O(3)^{iv}, 3.26 Å; C(1)···O(2)^{iii}, 3.18 Å; C(8)···O(3)^{v}, 3.30 Å; C(7)···O(6)^{iv}, 3.30 Å (symmetry transformations are given in footnote *a* of Table III; estimated standard deviations, 0.01 Å).

Description of the Complex Cation.—Perspective views of the complex are given in Figures 1 and 3.

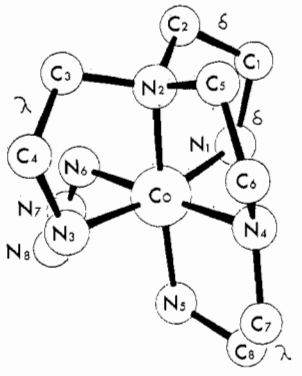

Figure 3.

Clearly, the tetraen ligand is not the linear form but a branched-chain isomer, 4-(2-aminoethyl)-1,4,7,10 tetraazadecane (abbreviated trenen). The ligand is coordinated quinquedentate in a symmetrical manner about the metal ion. If the puckering of the chelate rings is neglected, there is a mirror plane through the coordination plane containing the atoms N(2), N(4), N(5), N(6), and Co. For this reason the complex has been named[1] *sym*-$Co(trenen)N_3^{2+}$. Azide ion is coordinated to the metal ion at the remaining octahedral site.

An interesting feature of the complex cation is that the asymmetry of the ion is derived solely from the asymmetric secondary N atom, N(4). Inversion at this secondary N center produces the enantiomeric form of the complex. Also the chelate rings are puckered and the conformations are discussed in some detail later. Intramolecular bond distances and angles are given in Tables IV and V. With the exception of one bond all the Co^{III}–N bond distances are within 1σ of their mean value of 1.957 (3) Å. The Co–N(3) bond distance of 1.992 (5) Å is 7σ from this mean value. (Estimated standard deviations are given in parentheses right-adjusted to the least significant figure of the previous number.) This bond lengthening might be explained on the basis of unfavorable steric interactions between hydrogens on N(3) and hydrogens on the adjacent chelate rings. Clearly, the cobalt(III)–azide bond (1.957 (6) Å) is not significantly different from the cobalt(III)–amine mean value. However, it differs by 3σ from the cobalt(III)–azide distance of 1.943 (5) Å as found in the $[Co(NH_3)_5N_3](N_3)_2$ crystal structure.[11]

In the azido group the N–N bonds are not equivalent but are collinear and the bond angle to the metal ion is 119.0 (5)° compared with 124.8 (2)° in $Co(NH_3)_5N_3^{2+}$.[11] The unequal azide bonds in this complex, N(6)–N(7), 1.209 (7) Å, and N(7)–N(8), 1.152 (7) Å, are similar to those found in $Co(NH_3)_5N_3^{2+}$, being 1.208 (7) and 1.145 (7) Å, respectively.[11] In both structures the

(11) G. J. Palenik, *Acta Crystallogr.*, **17**, 360 (1964).

TABLE III
HYDROGEN BONDS IN THE $[Co(trenen)N_3](NO_3)_2 \cdot H_2O$ CRYSTAL[a]

Atoms X—H....Y	Atoms Y....H—X	d(X....Y) Å
O(7)—H....O(5)	O(5)....H—O(7)	2.94
O(7)—H....O(6)^{i}	O(6)....H—O(7)^{i}	3.01
C(6)—H....O(7)^{iii}	O(7)....H—C(6)^{ii}	3.16
N(1)—H....O(3)^{iv}	O(3)....H—N(1)^{vi}	2.90
N(1)—H....O(3)^{v}	O(3)....H—N(1)^{vii}	2.95
N(3)—H....O(5)^{viii}	O(5)....H—N(3)^{ix}	2.99
N(3)—H....O(6)^{vi}	O(6)....H—N(3)^{iv}	3.00
N(4)—H....O(2)^{v}	O(2)....H—N(4)^{vii}	2.98
N(5)—H....O(1)^{iv}	O(1)....H—N(5)^{vi}	3.00
N(5)—H....O(4)^{vi}	O(4)....H—N(5)^{iv}	3.04

Atoms	Angle (deg.)	Atoms	Angle (deg.)
O(7)....O(5)—N(10)	115	O(7)....O(6)^{i}—N(10)^{i}	122
O(7)....C(6)^{ii}—N(4)^{ii}	162	O(7)....C(6)^{ii}—C(5)^{ii}	90
N(1)....O(3)^{iv}—N(9)^{iv}	114	O(3)....N(1)^{vi}—Co^{vi}	115
O(3)....N(1)^{vi}—C(1)^{vi}	121	N(1)....O(3)^{v}—N(9)^{v}	109
O(3)....N(1)^{vii}—Co^{vii}	110	O(3)....N(1)^{vii}—C(1)^{vii}	107
O(5)....N(3)^{ix}—Co^{ix}	125	N(3)....O(5)^{viii}—N(10)^{viii}	104
N(3)....O(6)^{vi}—N(10)^{vi}	106	O(5)....N(3)^{ix}—C(4)^{ix}	102
O(6)....N(3)^{iv}—C(4)^{iv}	109	O(6)....N(3)^{iv}—Co^{iv}	112
O(2)....N(4)^{vii}—Co^{vii}	118	N(4)....O(2)^{v}—N(9)^{v}	111
O(2)....N(4)^{vii}—C(7)	107	O(2)....N(4)^{vii}—C(6)^{vii}	96
O(1)....N(5)^{vi}—Co^{vi}	113	N(5)....O(1)^{iv}—N(9)^{iv}	122
N(5)....O(4)^{vi}—N(10)^{vi}	127	O(1)....N(5)^{vi}—C(8)^{vi}	94
O(4)....N(5)^{iv}—C(8)^{iv}	109	O(4)....N(5)^{iv}—Co^{iv}	108

[a] Symmetry transformations: (i) $-x, 1-y, z$; (ii) $1-x, {}^1/_2+y, {}^1/_2-z$; (iii) $1-x, -{}^1/_2+y, {}^1/_2-z$; (iv) $-x, -{}^1/_2+y, {}^1/_2-z$; (v) $x, -1+y, z$; (vi) $-x, {}^1/_2+y, {}^1/_2-z$; (vii) $x, 1+y, z$; (viii) $x, {}^1/_2-y, {}^1/_2+z$; (ix) $x, {}^1/_2-y, -{}^1/_2+z$; (x) $1-x, 1-y, 1-z$.

TABLE IV
INTRAMOLECULAR DISTANCES FOR $[Co(trenen)N_3](NO_3)_2 \cdot H_2O$

Distances within $[Co(trenen)N_3]^{2+}$ cation

Atoms	Distance (Å)	Atoms	Distance (Å)
Co—N(1)	1.957(5)	N(2)—C(5)	1.510(9)
Co—N(2)	1.954(5)	C(3)—C(4)	1.509(9)
Co—N(3)	1.992(5)	N(3)—C(4)	1.499(8)
Co—N(4)	1.952(6)	C(5)—C(6)	1.536(10)
Co—N(5)	1.964(5)	N(4)—C(6)	1.452(8)
Co—N(6)	1.957(6)	N(4)—C(7)	1.483(8)
N(1)—C(1)	1.493(7)	C(7)—C(8)	1.520(10)
C(1)—C(2)	1.525(9)	N(5)—C(8)	1.477(9)
N(2)—C(2)	1.488(7)	N(6)—N(7)	1.209(7)
N(2)—C(3)	1.490(8)	N(7)—N(8)	1.152(7)

Distances within NO_3^- anions

N(9)—O(1)	1.238(7)	N(10)—O(4)	1.237(8)
N(9)—O(2)	1.257(6)	N(10)—O(5)	1.242(7)
N(9)—O(3)	1.252(7)	N(10)—O(6)	1.255(7)

azido group is coplanar with the metal ion and three other ligating nitrogen atoms. In the present structure the least sterically hindered orientation for the azido group would be midway between N(1) and N(5) rather than eclipsing the Co–N(5) bond. This feature of coordinated azide might be explained by a bonding requirement. If some π bonding occurred between the filled d_{xy} orbitals on the metal and the unfilled antibonding π orbitals of the azide ion, maximum orbital overlap would be obtained for an eclipsed configuration. Eclipsing of the azide ion with the Co–N(5) bond in the present structure involves less steric interaction than eclipsing with any of the other three Co–N bonds. However, more structural data are needed to establish this bonding requirement with certainty.

TABLE V
INTRAMOLECULAR BOND ANGLES FOR $[Co(trenen)N_3](NO_3)_2 \cdot H_2O$

Angles within $[Co(trenen)N_3]^{2+}$ cation

Atoms	Angle (deg.)	Atoms	Angle (deg.)
N(1)—Co—N(2)	86.9(2)	Co—N(2)—C(5)	109.1(4)
N(2)—Co—N(3)	84.7(2)	C(2)—N(2)—C(3)	111.1(5)
N(2)—Co—N(4)	87.0(2)	C(2)—N(2)—C(5)	111.0(5)
N(4)—Co—N(5)	85.6(2)	C(3)—N(2)—C(5)	111.9(5)
N(1)—Co—N(6)	87.3(2)	N(2)—C(3)—C(4)	107.7(5)
N(2)—Co—N(6)	93.5(2)	C(3)—C(4)—N(3)	108.5(5)
N(3)—Co—N(6)	86.7(2)	Co—N(3)—C(4)	111.1(3)
N(5)—Co—N(6)	94.0(2)	N(2)—C(5)—C(6)	111.7(5)
N(1)—Co—N(5)	94.8(2)	C(5)—C(6)—N(4)	107.3(5)
N(3)—Co—N(5)	94.4(2)	C(6)—N(4)—C(7)	117.4(5)
N(3)—Co—N(4)	94.6(2)	Co—N(4)—C(6)	109.1(4)
N(1)—Co—N(4)	91.5(2)	Co—N(4)—C(7)	109.3(4)
Co—N(1)—C(1)	110.5(3)	N(4)—C(7)—C(8)	107.0(5)
N(1)—C(1)—C(2)	107.7(5)	C(7)—C(8)—N(5)	108.8(6)
C(1)—C(2)—N(2)	108.1(5)	Co—N(5)—C(8)	110.9(4)
Co—N(2)—C(2)	106.9(3)	Co—N(6)—N(7)	119.0(5)
Co—N(2)—C(3)	106.6(4)	N(6)—N(7)—N(8)	176.4(9)

Angles within NO_3^- anions

O(1)—N(9)—O(2)	120.6(5)	O(4)—N(10)—O(5)	121.0(6)
O(1)—N(9)—O(3)	120.9(5)	O(4)—N(10)—O(6)	120.3(6)
O(2)—N(9)—O(3)	118.5(5)	O(5)—N(10)—O(6)	118.7(7)

The five-membered chelate rings subtend less than 90° angles at the metal ion (mean value 86.1 (1)°). These angular distortions mean that the coordination geometry cannot be strictly octahedral. Deviations of the ligating atoms and the metal ion from their mean coordination planes are given in Table VI.

TABLE VI
LEAST-SQUARES PLANES

(a) Equations of planes $AX + BY + CZ + D = 0$ where $X = ax$, $Y = by$, $Z = cz$,

Atoms included in plane	Plane No.	A	B	C	D
Co, N(1), N(4), N(3), N(6)	1	0.9583	0.2783	-0.0654	-0.8846
Co, N(2), N(4), N(5), N(6)	2	0.0059	-0.2167	-0.9762	10.3331
Co, N(1), N(2), N(3), N(5)	3	-0.3003	0.9272	-0.2240	-0.5566

(b) Distances of atoms from planes

Atoms	Deviations (Å) from Plane 1	Plane 2	Plane 3
Co	-0.06	0.00	0.01
N(1)	0.09	-	0.11
N(2)	-	-0.02	-0.13
N(3)	0.09	-	0.11
N(4)	-0.06	0.02	-
N(5)	-	-0.02	-0.11
N(6)	-0.07	0.02	-

Conformations of the Chelate Rings.—Figure 3 gives a perspective view of the chelate ring conformations and indicates the chirality of each puckered five-membered ring for that enantiomer. The chelate ring conformations are determined primarily by the configurations at the secondary nitrogen N(4) and the tertiary nitrogen N(2). The deviations of chelate ring carbon atoms from their respective N–Co–N planes and the dihedral angles about the C–C bonds are as follows: C(1), 0.07 Å; C(2), −0.56 Å; 47.0°; C(3), −0.75 Å; C(4), −0.18 Å, 43.8°; C(5), 0.13 Å; C(6), 0.64 Å, 38.5°; C(7), 0.51 Å; C(8), −0.11 Å, 45.4°. Clearly, the puckering of the chelate rings in all instances is very unsymmetrical. The small torsion angle (38.5°) about the C(5)–C(6) bond compares with the value (37.0°) found for the central chelate ring of trien in $Co(trien)ClOH_2^{2+}$.[3] This is not surprising since in the present structure the ligand can be considered as β-trien with an aminoethyl substituent at the "angular" nitrogen atom, N(2).

Chemical Significance of This Structure.—This structural analysis has revealed a new and interesting bifurcated quinquedentate ligand, 4-(2-aminoethyl)-1,4,-7,10-tetraazadecane (trenen). There are three other possible modes of coordination of this ligand about cobalt(III) and these are shown in Figure 4. Two of

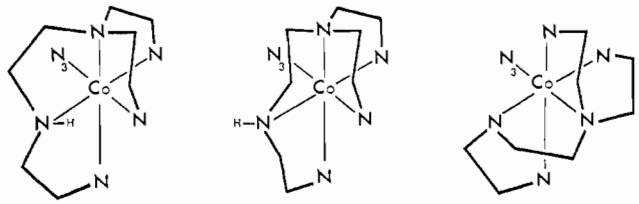

Figure 4.

these isomers are diastereoisomers (Figure 4a, b) differing only in the configuration at a "planar" asymmetric secondary N atom. Therefore, these two isomers are potentially interconvertible by inversion at this secondary N center. Two more $Co(trenen)N_3^{2+}$ isomers have been prepared and separated[1] on an ion-exchange column but they have not yet been isolated and chemically characterized.

As mentioned earlier, apart from the chelate ring conformations, the only source of asymmetry in the present complex, *sym*-$Co(trenen)N_3^{2+}$ is the asymmetric secondary N center, N(4) (Figure 3). Further, this site of asymmetry is trans to the substituent group. Hence this complex is particularly interesting from a kinetic and mechanistic viewpoint since removal of a proton from this secondary N center, by hydroxide ion, allows the complex to racemize and hydrolyze. Also this center will be the first to deprotonate since the proton is more acidic than any other N–H proton on the ligand by a factor of 10^5.

The rates and rate laws for base hydrolysis of a series of optically active *sym*-$Co(trenen)X^{2+}$ (where X^- = Cl^-, N_3^-) complexes were obtained.[12] These studies were carried out to examine the SN1CB mechanism and the possibility of a π-stabilized five-coordinate intermediate proposed for the base hydrolysis of these types of complexes.[13] It was shown[12] for the chloro complex that the base hydrolysis reaction path occurred with full retention of configuration. This result eliminated the possibility of forming a symmetrical five-coordinate intermediate in this system (see Figure 4). Retention is not too surprising since a symmetrical intermediate would involve conformational strain introduced by the eclipsing of all the protons for two coupled five-membered chelate rings (Figure 5).

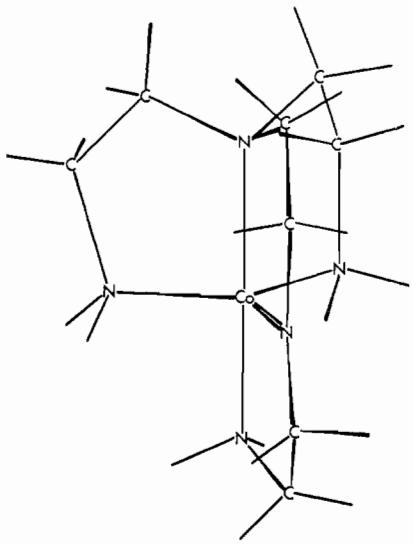

Figure 5.

Another interesting feature of the structure is that inversion at the secondary N center, N(4), must be synchronous with conformational interchange of the adjacent coupled chelate rings, in contrast to inversion in $Co(NH_3)_4Meen^{3+}$ (Meen = *N*-methylethylenediamine) where conformational interchange could precede or antecede the process. The synchronous conformational interchange is reflected in a higher retention ratio, k_{hex}/k_{inv}, in *sym*-$Co(trenen)N_3^{2+}$ (2.3×10^6) than in $Co(NH_3)Meen^{3+}$ (1.2×10^5).[14]

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(12) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **8**, 1595 (1969).

(13) R. G. Pearson and F. Basolo, *J. Amer. Chem. Soc.*, **78**, 4878 (1956).

(14) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **89**, 825 (1967).