

## Chiral Cobalt(III) Complexes of Symmetrical Hexaaza Macrocycles

D. J. ROYER,\* G. J. GRANT, D. G. VAN DERVEER, and M. J. CASTILLO

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The preparation of the symmetrical saturated hexaaza macrocycles 1,4,8,11,15,18-hexaazacycloheptacosane (21N6) and 1,4,7,10,13,16-tri-(*R,R*)-cyclohexano[*b,h,n*]hexaazacyclooctadecane (TC18N6) and their cobalt(III) complexes is reported. Co(21N6)<sup>3+</sup> was optically resolved, and evidence for two geometrical isomers was obtained. Column chromatography of the optically active Co(TC18N6)<sup>3+</sup> gave five geometric isomers, and some evidence for the existence of a sixth isomer was obtained. In addition the two chiral isomers of Co(18N6)<sup>3+</sup>, 18N6 = 1,4,7,10,13,16-hexaazacyclooctadecane, were optically resolved. Tentative structures can be assigned to most of the isomers on the basis of their chromatographic elution behavior and their circular dichroism spectra. With the 21-membered macrocycle the all-facial isomer of *D*<sub>3</sub> symmetry is the predominant isomer, while with both 18-membered macrocycles the "folded" isomer with approximate *D*<sub>2</sub> symmetry predominates. Unexpectedly, facile isomerization and racemization of the complexes were encountered, and no optically active crystals were isolated. However, racemic crystals of one isomer of Co(21N6)<sup>3+</sup> and one isomer of Co(18N6)<sup>3+</sup> were isolated and their structures determined: [Co(C<sub>15</sub>H<sub>36</sub>N<sub>6</sub>)](ClO<sub>4</sub>)<sub>3</sub>·H<sub>2</sub>O, space group *P*2<sub>1</sub>/*n*, with *a* = 13.033 (6) Å, *b* = 16.151 (7) Å, *c* = 12.184 Å, β = 94.21 (3)°, *V* = 2558.7 (2) Å<sup>3</sup>, *Z* = 4; [Co(C<sub>12</sub>H<sub>30</sub>N<sub>6</sub>)](ClO<sub>4</sub>)<sub>3</sub>·2H<sub>2</sub>O, space group *Pbcn*, with *a* = 13.09 (1) Å, *b* = 13.776 (8) Å, *c* = 13.626 (5) Å, *V* = 2457 (3) Å<sup>3</sup>, *Z* = 4. Intensities of 3795 (for the 21N6 complex) and 1660 (for the 18N6 complex) reflections were collected, and the structures were solved and refined by standard methods to *R* = 0.075 for the 21N6 complex and *R* = 0.069 for the 18N6 complex. The coordination geometry about the cobalt shows significant deviations from octahedral in both cases, especially in the case of the 21N6 complex. The structure and circular dichroism of Co(21N6)<sup>3+</sup> can be rationalized qualitatively by assuming that the five-membered chelate rings play a dominant role, with the six-membered chelate rings having little influence. With the Co(TC18N6)<sup>3+</sup> isomers the circular dichroism seems to be dominated by the conformationally rigid cyclohexane rings, with the ethylenediamine type rings playing a minor role. The observed circular dichroism spectra and the kinetically labile nature of the complexes are discussed.

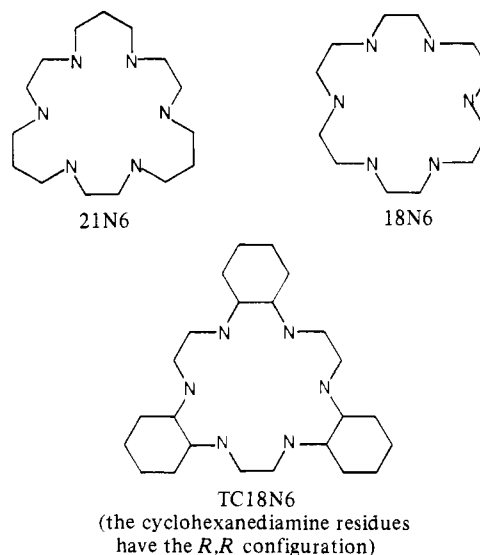
In contrast to the very large amount of work that has been done on the transition-metal complexes of tetraaza macrocycles in the last few years<sup>1</sup> there has been very little investigation of the complexes of macrocycles containing more than four potentially chelating nitrogens. There are a few scattered reports in the literature,<sup>1,2</sup> but they are generally rather fragmentary, and at the time that this work was undertaken, there were no reports in the literature involving potentially octahedral hexadentate macrocycles containing six sterically equivalent nitrogens.

A consideration of such systems indicated that saturated macrocycles containing approximately 18- to 21-membered rings should be of approximately the correct size and of sufficient flexibility to coordinate first-row transition metals in an octahedral fashion. cursory consideration indicated that, if such coordination were to occur, then a number of stereoisomers should be possible and that the majority of such stereoisomers should be chiral. This suggested that, if the macrocycles were properly chosen, in addition to the interesting stereochemistry involved, the circular dichroism of the compounds should be of considerable interest in its own right.

The origin of the rotatory strength associated with the d-d transitions in chiral transition-metal complexes and the relationship between the observed circular dichroism and the absolute configuration of the complexes are longstanding problems for which no completely satisfactory solutions have as yet appeared.<sup>3</sup> One of the problems has been a scarcity of suitable experimental systems in which to test unambiguously the predictions of the various theoretical models.<sup>4-8</sup>

Ideally such model systems should be of as high a symmetry as possible, they should be conformationally rigid so that solution spectra are meaningful, they should contain a minimum of unsaturation,<sup>9</sup> and they should be capable of providing a variety of widely different chiral environments of the metal. Macrocyclic complexes seemed to offer a reasonable chance of being very helpful in meeting all of the criteria, and so it was anticipated that it might be possible to interpret their CD spectra in a relatively unambiguous fashion.

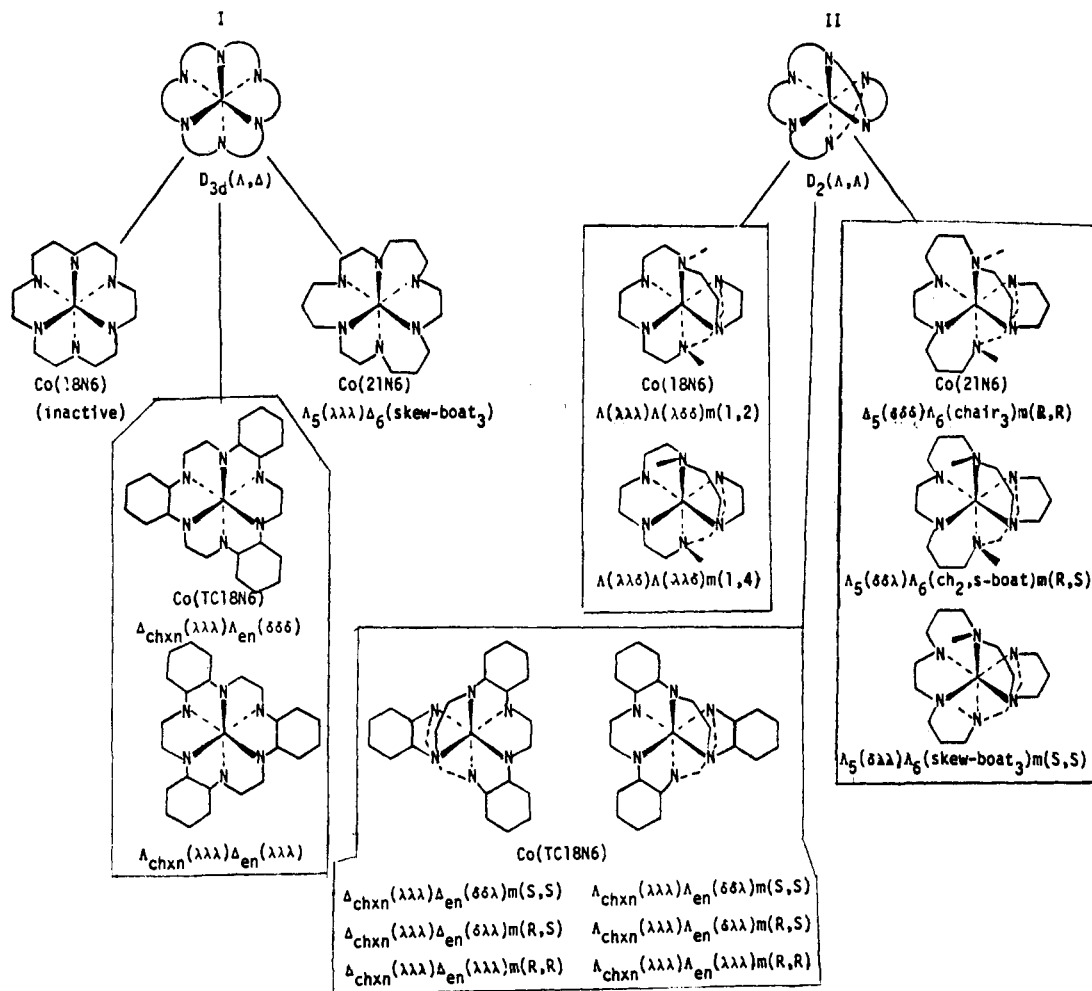
With these two objectives in mind, the investigation of the cobalt(III) complexes of the three macrocycles 21N6, 18N6,<sup>10</sup> and TC18N6 was undertaken. During the early phase of this



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investigation, the preparation and separation of the geometrical

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- (9) Moucharafieh, N. C.; Eller, P. G.; Bertrand, J. A.; Royer, D. *J. Inorg. Chem.* **1978**, *17*, 1220.
- (10) Yoshikawa<sup>11</sup> has used the trivial name hexaethylenhexamine for this macrocycle.



**Figure 1.** Stereochemistry of the hexaaza macrocyclic complexes. No attempt has been made to indicate the stereochemistry of the individual chelate rings in the drawings. This information is given in the designations assigned (see text of explanation of the nomenclature). The three designations given to each of the two isomers of Co(TC18N6) at the bottom of the figure are for the three possible orientations of the meridional imine hydrogens (see  $\Lambda, \Lambda$ -Co(21N6)).

isomers of  $\text{Co}(18\text{N}6)^{3+}$  were reported by Yoshikawa.<sup>11</sup> Our work on this system essentially complements the reported work.

The possible stereochemistry of flexible macrocyclic hexadentate complexes of the type being considered here is rather intricate, and there seems to be no generally accepted nomenclature that adequately describes the situation. The stereochemical possibilities and the nomenclature that we have adopted are illustrated in Figure 1. The nomenclature is essentially an extension of that used by Yoshikawa.<sup>11</sup>

If the nature of the linkages between the ligating atoms is not considered, other than the assumption that the linkages are short enough that no trans linkages will occur, two basic structures, in the configurational sense, are possible: structure I of approximate symmetry  $D_{3d}$  where all linkages are facial and the inherently chiral structure II of approximate symmetry  $D_2$  containing four facial linkages and two meridional linkages. We refer to these as the D3 configuration and the D2 configuration, respectively, without meaning to imply anything about the actual symmetry of a specific ion with one of these configurations.

The absolute configuration of one of these ions can be designated in the following way. The six chelate rings in the ion are broken into two sets by assigning the chelate rings alternately to each set as one proceeds around the macrocycle. Each set will then be arranged around a pseudo-3-fold axis in the same orientations as the three chelate rings in a *tris-*

bidentate complex. Thus each set of three alternate chelate rings can be designated as  $\Delta$  or  $\Lambda$ . In structures with the D2 configuration (structure II) the two sets will always have the same absolute configuration, and so the enantiomers of this type may be designated as  $\Delta\Delta$  and  $\Lambda\Lambda$  while structures with the D3 configuration would be designated as  $\Delta\Lambda$ . Information can then be appended to the  $\Delta$ 's and  $\Lambda$ 's to indicate the nature and conformation of the individual chelate rings in the same manner as is done for tris(bidentate) complexes. A unique designation could be given on that basis alone, but with the D2 configuration it is more convenient to consider the stereochemistry of the meridional imines. These two meridional imine linkages may have two possible orientations of the imine hydrogen, and as is well-known,<sup>12</sup> additional stereoisomers can arise from this source.

The designations for all of the feasible isomers of the complexes under consideration are given in Figure 1 (one member of each enantiomeric pair). The *mer*-(-,-) portion of the designations of the D2 isomers indicates the stereochemistry of the meridional imines. The conformations indicated for the individual chelate rings are essentially fixed by the overall stereochemistry in each case with very little flexibility.

Yoshikawa<sup>11</sup> has demonstrated the presence of all three isomers of  $\text{Co}(18\text{N}6)^{3+}$ . We report strong evidence for two of the four possible isomers of  $\text{Co}(21\text{N}6)^{3+}$  and weaker evidence for six of the eight isomers of  $\text{Co}(\text{TC}18\text{N}6)^{3+}$ .

(11) Yoshikawa, Y. *Chem. Lett.* 1978, 109.

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Table I. Summary of Crystallographic Data

|   | Co(C <sub>15</sub> H <sub>36</sub> N <sub>6</sub> )-<br>(ClO <sub>4</sub> ) <sub>3</sub> ·H <sub>2</sub> O | Co(C <sub>12</sub> H <sub>30</sub> N <sub>6</sub> )-<br>(ClO <sub>4</sub> ) <sub>3</sub> ·2H <sub>2</sub> O |
|---|--|---|
| space group   | <i>P</i> 2 <sub>1</sub> / <i>n</i>   | <i>Pbcn</i>   |
| <i>a</i> , Å  | 13.033 (6)   | 13.09 (1)   |
| <i>b</i> , Å  | 16.151 (7)   | 13.776 (8)  |
| <i>c</i> , Å  | 12.184 (5)   | 13.626 (5)  |
| β, deg  | 94.21 (3)  |   |
| <i>V</i> , Å <sup>3</sup>   | 2558.7 (2)   | 2457 (3)  |
| <i>d</i> <sub>calc</sub> , <i>d</i> <sub>obsd</sub> , g/cm <sup>3</sup> | 1.75, 1.70   | 1.77, 1.75  |
| <i>Z</i>  | 4  | 4   |
| no. of variables  | 274  | 152   |
| no. of observns   | 3795   | 1660  |
| <i>R</i>  | 0.075  | 0.069   |
| <i>R</i> <sub>w</sub>   | 0.078  | 0.070   |
| largest peak, <sup>a</sup> e/Å <sup>3</sup>                             | 1.01   | 0.76  |
| Δ/σ <sup>b</sup>  | 0.23   | 0.14  |

<sup>a</sup> Largest peak in the final difference Fourier. <sup>b</sup> Largest parameter shift per parameter estimated deviation in the last cycle of least-squares refinement.

### Experimental Section

**Materials and Methods.** The 18N6·3H<sub>2</sub>SO<sub>4</sub> used was generously supplied by Professor Jack E. Richman. All other chemicals were of the best commercially available grade and were used without further purification.

Visible and UV spectra were obtained with a Cary 14 spectrophotometer, circular dichroism spectra were obtained with a JASCO ORD/CD-5 spectrometer, and <sup>13</sup>C spectra were recorded on a JEOL Fourier transform NMR spectrometer.

**Preparation of 21N6 and TC18N6.** Both of the macrocycles were prepared by suitable adaptations of the Richman procedure.<sup>13</sup> 21N6 was prepared by the cyclization of tosylated 1,10-diamino-4,7-diazadecane<sup>14</sup> and 1,9-dihydroxy-3,7-diazanonane.<sup>15</sup>

**TC18N6.** *trans*-Cyclohexanediamine was resolved by fractional crystallization of the *d*-tartrate salt, and the *R,R* isomer was used in all preparations. *N,N'*-Bis(2-aminocyclohexyl)-1,2-diaminoethane was prepared by reaction of 1,2-dibromoethane with an 8-fold excess of cyclohexanediamine. Some cyclization occurred, but workup gave the desired product in about 50% yield. *N,N'*-Bis(2-hydroxyethyl)-*N,N'*-ditosylcyclohexanediamine was prepared by the reaction of the disodium salt of *N,N'*-ditosylcyclohexanediamine with 2-bromoethanol in ethanol. The two precursors were then tosylated and cyclized in a normal Richman reaction. Workup gave approximately 30% yield of the desired product. <sup>13</sup>C{<sup>1</sup>H} NMR (D<sub>2</sub>O): δ 28.8, 30.3, 53.1, 57.1.

**Preparation of the Cobalt(III) Complexes.** All of the complexes were prepared by the method of Bauer and Drinkard<sup>16</sup> using Na<sub>3</sub>[Co(CO<sub>3</sub>)<sub>3</sub>]·3H<sub>2</sub>O.

**Chromatography.** The isomer separations and the optical resolutions were all carried out with a 180 × 2 cm column of SP-Sephadex C-25 in the sodium form. Co(21N6)<sup>3+</sup> was resolved by eluting with an acidified (pH 3–5) 0.3 M sodium tartrate solution and the resolution monitored by following the Kuhn dissymmetry factor (CD)/absorbance for the low-energy (T<sub>1g</sub>) transition. The enantiomer with net positive *R* (rotational strength) eluted first. The leading portion of the band had to be recycled through the column three times before a constant dissymmetry factor was obtained. Repeated attempts to separate isomers of Co(21N6)<sup>3+</sup> by a number of different elution conditions failed.

The geometrical isomers of the optically active Co(TC18N6)<sup>3+</sup> were separated by elution with acidified (pH 3–5) 0.12 M sodium sulfate solution.

The geometrical isomers of Co(18N6)<sup>3+</sup> were separated as described by Yoshikawa<sup>11</sup> and the chiral isomers resolved by two passes through the column with acidified 0.3 M sodium tartrate.

**Collection and Reduction of the X-ray Data.** A Syntex P2<sub>1</sub> four-circle diffractometer equipped with a graphite monochromator (Bragg

Table II. Atomic Coordinates for Co(C<sub>15</sub>H<sub>36</sub>N<sub>6</sub>)(ClO<sub>4</sub>)<sub>3</sub>·H<sub>2</sub>O

| atom | <i>x</i>     | <i>y</i>    | <i>z</i>    |
|------|--------------|-------------|-------------|
| Co   | -0.01696 (6) | 0.27193 (5) | 0.73011 (4) |
| N1   | 0.0190 (4)   | 0.2225 (3)  | 0.8703 (40) |
| N2   | 0.0467 (4)   | 0.3813 (3)  | 0.7785 (4)  |
| N3   | -0.1535 (4)  | 0.3179 (3)  | 0.7640 (4)  |
| N4   | 0.1195 (4)   | 0.2305 (3)  | 0.6934 (4)  |
| N5   | -0.0283 (4)  | 0.3252 (3)  | 0.5883 (4)  |
| N6   | -0.1002 (4)  | 0.1737 (3)  | 0.6739 (4)  |
| C1   | -0.0339 (5)  | 0.1441 (4)  | 0.9014 (5)  |
| C2   | -0.0331 (6)  | 0.0760 (4)  | 0.8221 (6)  |
| C3   | -0.1108 (6)  | 0.0918 (5)  | 0.7301 (6)  |
| C4   | -0.2069 (5)  | 0.2082 (4)  | 0.6475 (5)  |
| C5   | -0.2357 (5)  | 0.2555 (4)  | 0.7409 (6)  |
| C6   | -0.1623 (6)  | 0.3555 (4)  | 0.8690 (6)  |
| C7   | -0.0963 (6)  | 0.4315 (5)  | 0.8867 (7)  |
| C8   | 0.0166 (5)   | 0.4173 (5)  | 0.8802 (6)  |
| C9   | 0.0311 (5)   | 0.4432 (4)  | 0.6926 (6)  |
| C10  | 0.0401 (5)   | 0.3993 (4)  | 0.5920 (5)  |
| C11  | -0.0103 (5)  | 0.2741 (5)  | 0.4925 (5)  |
| C12  | 0.0931 (6)   | 0.2334 (5)  | 0.4986 (6)  |
| C13  | 0.1240 (6)   | 0.1812 (4)  | 0.5939 (5)  |
| C14  | 0.1737 (5)   | 0.1837 (5)  | 0.7829 (5)  |
| C15  | 0.1326 (5)   | 0.2145 (4)  | 0.8822 (6)  |
| Cl1  | 0.2511 (1)   | 0.0216 (1)  | 0.0311 (1)  |
| O1,1 | 0.1588 (4)   | 0.0022 (4)  | -0.0268 (5) |
| O1,2 | 0.2316 (6)   | 0.0809 (4)  | 0.1090 (6)  |
| O1,3 | 0.2925 (5)   | -0.0510 (4) | 0.0800 (5)  |
| O1,4 | 0.3230 (4)   | 0.0564 (4)  | -0.0343 (6) |
| O2,1 | -0.0124 (1)  | 0.3138 (1)  | 0.1715 (1)  |
| O2,2 | 0.0386 (6)   | 0.2820 (6)  | 0.0893 (5)  |
| O2,3 | -0.0992 (6)  | 0.3577 (7)  | 0.1374 (9)  |
| O2,4 | -0.0311 (8)  | 0.2499 (6)  | 0.2384 (6)  |
| O2,5 | 0.0602 (7)   | 0.3673 (6)  | 0.2270 (8)  |
| O3,1 | 0.3268 (2)   | 0.4489 (1)  | 0.9161 (2)  |
| O3,2 | 0.2679 (8)   | 0.3757 (6)  | 0.9070 (8)  |
| O3,3 | 0.4212 (7)   | 0.4225 (7)  | 0.9542 (9)  |
| O3,4 | 0.332 (1)    | 0.4849 (5)  | 0.8224 (6)  |
| O3,5 | 0.294 (1)    | 0.5045 (6)  | 0.9895 (8)  |
| O    | 0.2824 (5)   | 0.3465 (5)  | 0.6616 (7)  |

2θ angle = 12.2°) using Mo Kα radiation at a takeoff angle of 6.75° was used. Identical X-ray source and monochromator settings were used in the determination of the unit cell parameters and the orientation matrix and in the collection of the intensity data.

[Co(21N6)](ClO<sub>4</sub>)<sub>3</sub>·H<sub>2</sub>O ([Co(C<sub>15</sub>H<sub>36</sub>N<sub>6</sub>)](ClO<sub>4</sub>)<sub>3</sub>·H<sub>2</sub>O). A red octahedral crystal with approximate dimensions 0.65 × 0.30 × 0.25 mm was grown by slow evaporation of an aqueous solution (5 days). The unit cell parameters are given in Table I. A total of 5204 reflections were collected in a complete quadrant of data at 2θ = 50°; 3797 were accepted as statistically above background on the basis of *F* was greater than 3[σ(*F*)].

Computations were performed with use of standard programs;<sup>17</sup> all computations were carried out on the CDC Cyber 74 system. For structure factor calculations the scattering factors were taken from Cromer and Waber's tabulation.<sup>18</sup> The scattering factors for all atoms except hydrogen were corrected for real and imaginary anomalous dispersion components.<sup>19</sup> The agreement factors are defined in the usual way as

$$R = (\sum ||F_o| - |F_c||) / (\sum |F_o|)$$

$$R_w = \sum (|F_o| - |F_c|)(w^{1/2}) / \sum (|F_o|)(w^{1/2})$$

A weighting scheme based on counting statistics ( $w = 2.72 / [\sigma(F)]^2 + 0.0006F^2$ ) was employed for the calculation of *R*<sub>w</sub> and in least-squares refinement.

The positions of the cobalt and the chlorines were located from a Patterson map, and the positions of the remaining nonhydrogen atoms were located by a series of difference Fourier maps. The structure was refined to the residuals given in Table I. The final atomic coordinates of the nonhydrogen atoms are given in Table II, and some

(13) Richman, J. E.; Atkins, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 2268.

(14) Bosnich, B.; Harrowfield, J. M.; Boucher, H. *Inorg. Chem.* **1975**, *14*, 815.

(15) Nelson, E. R.; Maionthal, J. M.; Lane, L. A.; Benderly, A. A. *J. Am. Chem. Soc.* **1957**, *79*, 3467.

(16) Bauer, H. F.; Drinkard, W. C. *J. Am. Chem. Soc.* **1960**, *82* 5031.

(17) Programs utilized were Sheldrick's SHELX-76 program and Johnson's ORTEP program.

(18) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–101.

(19) Reference 18, Vol. IV, pp 149–150.

Table III. Selected Distances (Å) and Angles (Deg) for  $\text{Co}(\text{C}_{15}\text{H}_{36}\text{N}_6)^{3+}$ 

|          |           |           |           |
|----------|-----------|-----------|-----------|
| Co-N1    | 1.913 (5) | Co-N5     | 1.926 (5) |
| Co-N2    | 2.021 (5) | Co-N6     | 2.013 (5) |
| Co-N3    | 1.999 (5) | C-N av    | 1.47 (2)  |
| Co-N4    | 1.982 (5) | C-C av    | 1.47 (3)  |
| N1-Co-N4 | 84.0 (2)  | N1-Co-N5  | 170.2 (2) |
| N4-Co-N5 | 87.8 (2)  | N2-Co-N6  | 170.9 (2) |
| N5-Co-N2 | 82.8 (2)  | N3-Co-N4  | 177.7 (2) |
| N2-Co-N3 | 88.2 (2)  | Co-N-C av | 114 (6)   |
| N3-Co-N6 | 84.1 (2)  | N-C-C av  | 111 (4)   |
| N6-Co-N1 | 93.7 (2)  | C-C-C av  | 112 (2)   |

Table IV. Atomic Coordinates for  $\text{Co}(\text{C}_{12}\text{H}_{30}\text{N}_6)(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ 

| atom | x           | y           | z          |
|------|-------------|-------------|------------|
| Co   | 0.0000      | 0.25098 (7) | 0.25000    |
| N1   | 0.0978 (4)  | 0.2463 (4)  | 0.1425 (4) |
| N2   | 0.0876 (4)  | 0.3564 (3)  | 0.3016 (4) |
| N3   | -0.0688 (4) | 0.1469 (3)  | 0.1754 (4) |
| C1   | 0.1692 (6)  | 0.3276 (5)  | 0.1448 (5) |
| C2   | 0.1860 (5)  | 0.3647 (5)  | 0.2464 (5) |
| C3   | 0.0334 (5)  | 0.4514 (5)  | 0.2920 (5) |
| C4   | 0.0443 (6)  | 0.2240 (5)  | 0.0530 (5) |
| C5   | -0.0265 (6) | 0.1425 (5)  | 0.0737 (6) |
| C6   | -0.0530 (5) | 0.0544 (4)  | 0.2285 (5) |
| Cl1  | 0.0000      | -0.2214 (2) | 0.25000    |
| Cl2  | 0.2127 (1)  | 0.4219 (1)  | 0.5286 (1) |
| O1   | 0.2320 (5)  | 0.4160 (5)  | 0.6295 (4) |
| O2   | 0.1244 (5)  | 0.4717 (5)  | 0.5091 (5) |
| O3   | 0.2063 (5)  | 0.3273 (4)  | 0.4890 (4) |
| O4   | 0.2928 (7)  | 0.4704 (6)  | 0.4854 (4) |
| O5   | -0.051 (2)  | -0.167 (2)  | 0.325 (1)  |
| O6   | -0.023 (1)  | -0.3106 (9) | 0.214 (2)  |
| O7   | -0.071 (2)  | -0.234 (2)  | 0.183 (1)  |
| O8   | -0.082 (1)  | -0.179 (2)  | 0.266 (4)  |
| O    | 0.2809 (4)  | 0.1388 (4)  | 0.3610 (5) |

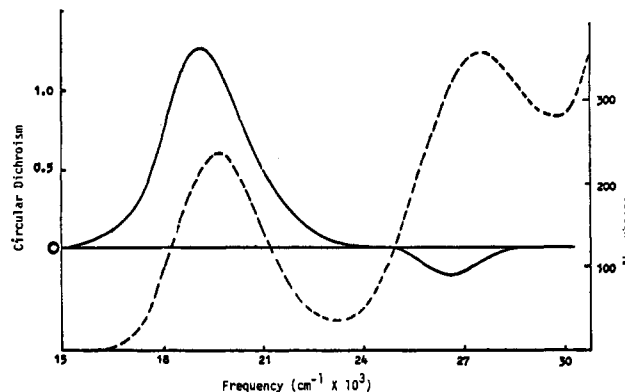
Table V. Distances (Å) and Angles (Deg) for  $\text{Co}(\text{C}_{12}\text{H}_{30}\text{N}_6)^{3+}$ 

|           |           |           |            |
|-----------|-----------|-----------|------------|
| Co-N1     | 1.947 (5) | C-N av    | 1.47 (2)   |
| Co-N2     | 1.979 (5) | C-C av    | 1.47 (3)   |
| Co-N3     | 1.975 (5) |           |            |
| N1-Co-N2  | 84.9 (2)  | N2-Co-N3  | 168.4 (2)  |
| N1-Co-N3  | 83.6 (2)  | N1-Co-N1' | 176.2 (3)  |
| N2-Co-N2' | 85.6 (3)  | Co-N-C av | 109.6 (13) |
| N3-Co-N3' | 86.9 (3)  | N-C-C av  | 110 (2)    |

distances and angles are given in Table III. Thermal parameters, hydrogen positions, and a list of calculated and observed structure factors are available.<sup>20</sup> The temperature factors of a number of the perchlorate oxygens would seem to indicate that there is probably unresolved disorder associated with all of the perchlorate ions (especially perchlorate 3). This is supported by the observation that the six highest peaks in the final difference Fourier were associated with the perchlorate ions. The largest peak associated with the cation ( $0.6 \text{ e}/\text{Å}^3$ ) was located midway between carbon 14 and carbon 15. The apparent disorder in the perchlorate ions is probably responsible for the rather high residuals, but because it did not seem to be affecting the cation significantly, it was left unresolved.

$[\text{Co}(\text{18N6})](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$  ( $[\text{Co}(\text{C}_{12}\text{H}_{30}\text{N}_6)](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ ). The collection of the data, the solution of the structure, and the refinement were essentially the same as described for  $[\text{Co}(\text{21N6})](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ . A total of 13 reflections ( $2\theta = 5.21\text{--}14.57^\circ$ ) were used in the determination of the lattice parameters (Table I). A total of 2491 reflections were collected in a complete octant out to  $2\theta = 50^\circ$  of which 1660 were accepted as statistically above background. The final refined atomic coordinates are given in Table IV, and some distances and angles are given in Table V. Thermal parameters, hydrogen positions, and a list of calculated and observed structure factors are available.<sup>20</sup>

Again the perchlorate oxygen thermal parameters seem to indicate some unresolved disorder in the perchlorate ions. The largest peak

Figure 2. Visible and CD spectra of  $\Delta_5(\lambda\lambda\lambda)\Delta_6(\text{skew boat})_3\text{-Co}(21\text{N6})^{3+}$ .

in the final difference Fourier associated with the cation ( $0.57 \text{ e}/\text{Å}^3$ ) was  $0.7 \text{ Å}$  from carbon 3.

## Results and Discussion

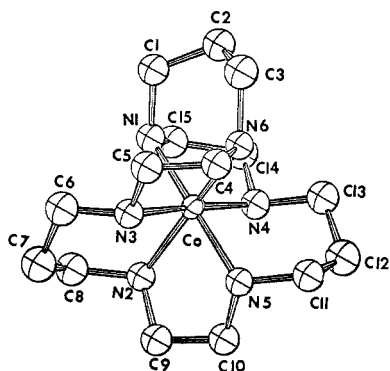
$\text{Co}(21\text{N6})^{3+}$ . Elution of  $\text{Co}(21\text{N6})^{3+}$  from a SP-Sephadex chromatography column gave essentially a single band with no evidence for isomer separation. The material gave a sharp three-line  $^{13}\text{C}\{\text{H}\}$  NMR spectrum (in  $\text{D}_2\text{O}$ ),  $\delta$  43.59, 49.99, and 55.20, consistent only with the symmetrical  $D_3$  isomer. Optical resolution of this material gave the CD spectrum given in Figure 2. This spectrum, which is strongly reminiscent of that of  $\Lambda\text{-Co}(\text{en})_3^{3+}$  in the  $T_{1g}$  region, is essentially what would be expected for the  $\Delta_5\Delta_6$  enantiomer if the conformation of the complex and thus the circular dichroism are primarily determined by the five-membered rings. The only real difference is that this spectrum lacks the small negative component seen in  $\Lambda\text{-Co}(\text{en})_3^{3+}$ . An attempt was made to bring out this a band by the gengen effect.<sup>4</sup> However, the spectrum taken in sodium phosphate solution was virtually unchanged in the  $T_{1g}$  region. This would seem to support the point of view that the gengen effect operates by generating chirality in the nitrogens since, in this case where the nitrogens are already chiral, no effect is seen.

The material retains its optical activity unchanged in the solid state as the chloride salt, but significant loss of activity was observed in solution within 1 week, and solutions eventually became totally inactive. This seems to be due to racemization and not due to decomposition because the absorption spectrum was completely unchanged over the same time period.

Attempts were made to grow X-ray crystals of the active material, but usable crystals were obtained only by slow (about 5 days) evaporation of an aqueous solution, and the recovered crystals were invariably racemic. Crystals of the perchlorate salt and of the tetrachlorozincate salt were examined, but since the two salts contained the same geometrical isomer of the cation in essentially the same conformation, the crystallographic data is reported only for the perchlorate salt. The geometrical isomer found in the salt is not the principal isomer in solution. The  $^{13}\text{C}$  NMR spectrum of the solution is not consistent with the solid-state structure. Apparently an isomer that was present in rather small amounts in an equilibrium mixture in solution was the one that crystallized out. We estimate that this second isomer would have been seen in the NMR spectrum if its concentration in solution was greater than about 5% of the total. The isomer isolated is the one with the  $(\Delta\Delta)_5(\text{lel})_3(\Delta\Delta)_6(\text{chair})_3$  conformation. A drawing of the cation is shown in Figure 3, and some distances and angles are given in Table IV. There are no unusually short cation-anion distances in the crystal, and the only significant hydrogen bonding is a rather long bond involving nitrogen 4 and the water of hydration ( $2.9 \text{ Å}$ ). Thus the observed conformation

(20) Supplementary material.

(21) Mason, S. F.; Norman, B. J. *J. Chem. Soc. A* 1966, 307.



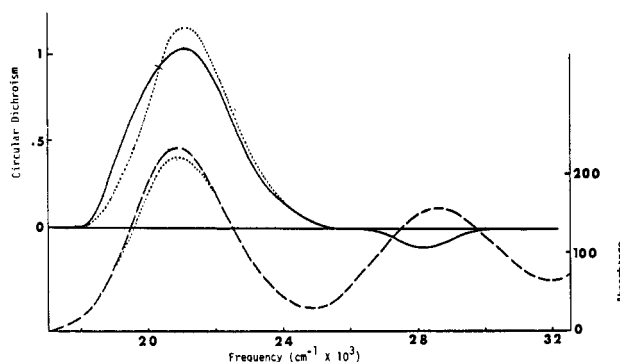
**Figure 3.** Structure of the cation in *rac*-Co(21N6)(ClO<sub>4</sub>)<sub>3</sub>·H<sub>2</sub>O. The drawing is of the  $\Lambda_5(\delta\delta\delta)\Delta_6(\text{chair})_3\text{-mer-(R,R)}$  enantiomer.

seems to be essentially that imposed by the steric demands of the ligand. The N–Co–N angles associated with the five-membered chelate rings are 82.8, 84.0, and 84.1° while those associated with the six-membered chelate rings are 87.7, 88.2, and 93.7°, which are not unusual for angles of these types. In addition, the dihedral angles in the five-membered rings are quite normal and two of the three six-membered rings show only moderate deviation from the normal chair form. Only the six-membered ring at the top of the drawing shows considerable distortion and thus significant strain. However, considerable steric strain is indicated by the Co–N distances, which range from 1.91 to 2.01 Å.

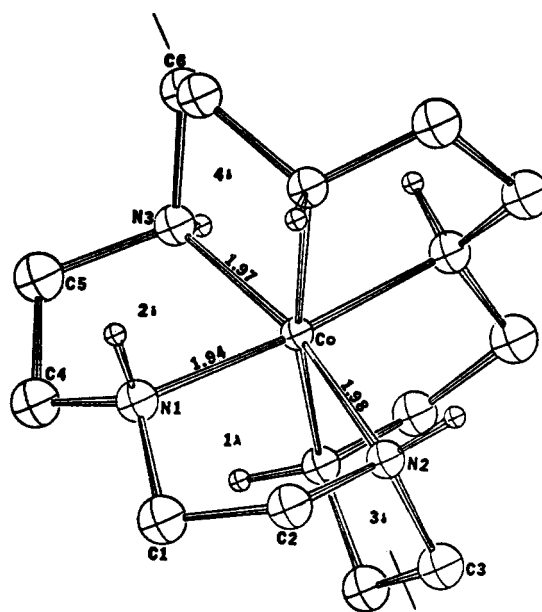
An examination of models seems to indicate that the observed stereoisomer with the 5(1e1)<sub>3</sub>,6(chair)<sub>3</sub> conformation is probably the lowest energy of the three feasible stereoisomers of general configuration D<sub>2</sub> that can be generated by altering the chirality of the meridional imines.

This result inspired renewed attempts to isolate minor isomers out of the Co(21N6)<sup>3+</sup> solution. Repeated attempts using a number of different eluting agents at different concentrations were unsuccessful. The difficulty seems to be that the empirical elution rules,<sup>22</sup> which seem to have wide validity, indicate that the symmetrical  $\Lambda\Delta$  isomer should elute first. In this case, this is the isomer that is present in high concentration. Thus any other isomers present in small amount would have eluted after the large main band, and the tailing of the main band, which always occurs, would make the detection of small trailing bands difficult. Thus we cannot rule out the presence of small amounts of the other isomers in solution on the basis of chromatographic evidence. However, since the time required to grow crystals was comparable to the racemization time of the solution and since these complexes can apparently only isomerize by a series of isomerization steps (vide infra), the time required must be at least comparable to the time required to establish equilibration of the isomers in solution, and so the isomer that crystallized out need not have been present in large amounts.

**Co(18N6)<sup>3+</sup>.** Our chromatographic results confirm the observations of Yoshikawa<sup>11</sup> that an equilibrium mixture of this material consists of a small amount (<1%) of the achiral *D*<sub>3d</sub> isomer and an approximately equal mixture of the two chiral isomers of the D<sub>2</sub> configuration (actual symmetry C<sub>2</sub>). The CD spectra are shown in Figure 4. As would be expected, the two curves are very similar, and again the rotation in the T<sub>1g</sub> band is quite reminiscent of that of  $\Lambda$ -Co(en)<sub>3</sub><sup>3+</sup>. The sign of this band, plus the general observation that  $\Lambda$  isomers are usually eluted ahead of  $\Delta$  isomers with *d*-tartrate, would seem to indicate that these are the  $\Lambda\Lambda$  isomers. The analogy would seem to indicate that we are seeing a component of the band



**Figure 4.** Visible and CD spectra of the two active isomers of Co(18N6)<sup>3+</sup>. The solid line is the isomer that eluted first from the column.

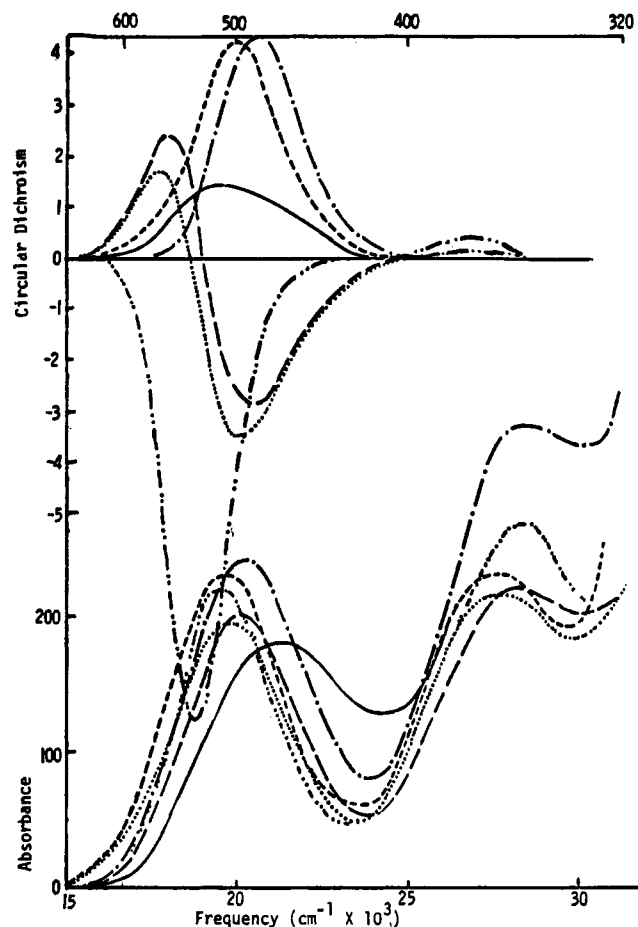


**Figure 5.** Structure of the cation in *rac*-Co(18N6)(ClO<sub>4</sub>)<sub>3</sub>·2H<sub>2</sub>O. The drawing is the  $\Delta(\delta\delta\delta)\Delta(\lambda\lambda\delta)\text{-mer-(1,2)}$  enantiomer.

that resembles the *e* component of Co(en)<sub>3</sub><sup>3+</sup> despite the fact that the molecule lacks a 3-fold axis.<sup>23</sup>

Repeated attempts to isolate optically active crystals using different conditions and different gegenions were unsuccessful. The only crystals of X-ray quality that were obtained resulted from very slow (several weeks) growth from aqueous perchlorate media, and such crystals were invariably racemic. Unfortunately, this implies that there is no way to relate the structure observed in the crystal to that of one of the isomers in solution. The structure of the isomer is given in Figure 5, and some distances and angles are given in Table V. This is the isomer designated *rac*-2 by Yoshikawa.<sup>11</sup> There are no unusual cation–anion distances in the structure, and the only appreciable hydrogen bonding is a rather long bond (2.8 Å) between the water of hydration and nitrogen 3. The cation lies on a crystallographic 2-fold axis so that the C<sub>2</sub> symmetry predicted for the isolated cation is retained in the crystal. The observed conformation of the cation seems to be essentially that dictated by the steric demands of the ligand. The nominally 90° N–Co–N angles involved in the five-membered chelate rings range from 83 to 87° while those not involved in the chelate rings range from 93 to 99°. The slight short-

(23) The situation is probably worse than indicated, because the work of Richardson<sup>8</sup> indicates that the conventional separation of these bands into two or three components is probably not justified even in the tris(bidentate) complexes.



**Figure 6.** Visible and CD spectra of various isomers of  $\text{Co}(\text{TC18N6})^{3+}$ : (—) band I,  $\Delta_{\text{chxn}}(\lambda\lambda\lambda)\Delta_{\text{en}}(\delta\delta\delta)$ ; (···) band IIa,  $\Delta_{\text{chxn}}(\lambda\lambda\lambda)\Delta_{\text{en}}(\delta\delta\lambda)\text{-mer-}(S,S)$ ; (---) band IIb,  $\Delta_{\text{chxn}}(\lambda\lambda\lambda)\Delta_{\text{en}}(\delta\delta\lambda)\text{-mer-}(S,S)$ ; (-·-·) band IIIa,  $\Delta_{\text{chxn}}(\lambda\lambda\lambda)\Delta_{\text{en}}(\delta\lambda\lambda)\text{-mer-}(R,S)$ ; (---) band IIIb,  $\Delta_{\text{chxn}}(\lambda\lambda\lambda)\Delta_{\text{en}}(\delta\lambda\lambda)\text{-mer-}(R,S)$ ; (-·-·) X (see text). The assignments are considered to be only tentative.

ening of the N1–Co bond (1.94 Å) and the slight movement of N2 and N3 in the direction of N1 (N2–Co–N3 angle = 168°) would be expected on the basis of the meridional linkage at N1.<sup>24</sup>

This lack of solid-state effects is confirmed by the rather remarkable agreement between the observed structure and the results of the conformational analysis calculation carried out by Yoshikawa.<sup>25</sup> A detailed comparison shows that the calculated bond distances all agree with the observed distances within  $\pm 0.02$  Å, the bond angles agree within  $\pm 1.0^\circ$ , and the N–C–C–N dihedral angles agree within  $\pm 3^\circ$ .

**Co(TC18N6)<sup>3+</sup>.** This material proved to be rather labile with respect to both isomerization and decomposition. Solutions of the complex showed visible decomposition within 1 hour when the solution pH was less than 1 or greater than 7. The solutions did not decompose at an appreciable rate in the pH range from 2 to 4.

Chromatography gave three well-defined bands: a very small leading band (band I, <1% of the material), a second band (band II, ~30% of the material), and a large third band (band III, ~70% of the material). The CD spectra of the second and third bands showed that they both consisted of two overlapping bands with quite different CD spectra. The observed CD spectra are given in Figure 6. The a and b spectra

of bands II and III are the leading and trailing edges of the band, respectively. All five of these separated materials isomerized in solution under ambient laboratory conditions with half-times of 3–6 days to give the originally observed mixture of isomers (determined by monitoring the CD spectra and rechromatographing the isomerized materials individually).

The spectrum marked X in Figure 6 is that of a sample of band III that had been stripped to dryness in the form that it was eluted from the column and stored in a vacuum desiccator for approximately 2 months. This material, which clearly must contain something other than the five materials observed in the original separation, reverted to the original mixture of isomers without appreciable decomposition upon standing in solution for 3 days.

The identification of these isomers, even on a very tentative basis, is not straightforward, but some reasonable assignments can be made. The assignment of band I to one of the two possible isomers of D3 configuration is consistent with its elution position, its absorption spectrum, and its low rotation. Of these two, the  $\Delta_{\text{chxn}}(\lambda\lambda\lambda)\Delta_{\text{en}}(\delta\delta\delta)$  isomer seems the most probable on the basis of the observation that the  $(\text{le})_3$  form of  $\text{Co}(\text{chxn})_3^{3+}$  is of considerably lower energy than the  $(\text{ob})_3$  form.<sup>26</sup>

The signs and general shapes of the CD curves would seem to clearly suggest that bands II and III each contain one  $\Delta\Delta$  and one  $\Lambda\Lambda$  isomer. The b subbands, which have simple positive bands in the  $T_{1g}$  region, can be assigned to the  $\Lambda\Lambda$  structure by analogy to the spectra of the other macrocycles. This leads to the assignments of the a subbands as having the  $\Delta\Delta$  structure. This is reasonable in that the  $\Delta\Delta$  structures would be expected to have predominantly negative curves.

The assignment of the stereochemistry of the *mer* imines given in Figure 6 was made on the basis of an examination of models and is considered to be very tentative. There seems to be a considerable difference in the strain introduced into the coordination octahedron of the cobalt by the different arrangements of the *mer* imines with little apparent change in the rest of the molecule. The *mer*-(S,S) arrangement seems to give the least strain in both the  $\Delta\Delta$  and the  $\Lambda\Lambda$  structures. The *mer*-(R,S) arrangement seems to increase the strain somewhat, and the *mer*-(R,R) arrangement seems to rather severely distort the octahedron. Therefore, the most abundant isomers are tentatively assigned the *mer*-(S,S) configuration, and the isomers apparently not seen are assumed to be the ones with the *mer*-(R,R) configuration.

The identity of the material labeled X is not clear; it may be the  $\Delta_{\text{chxn}}(\lambda\lambda\lambda)\Delta_{\text{en}}(\lambda\lambda\lambda)$  isomer (the Kuhn dissymmetry factor is very close to that of  $\text{ob-Co}(\text{chxn})_3^{3+}$ ).<sup>26</sup>

Repeated attempts to crystallize any of the isomers of  $\text{Co}(\text{TC18N6})$  from a variety of solvents and with a variety of counterions were not successful.

**Mechanism of the Racemizations and Isomerizations.** The unexpectedly facile isomerizations and racemizations observed in all three of these systems deserves some consideration. There is clearly considerable steric strain in all of these systems. Yoshikawa<sup>11</sup> calculates 140 kJ/mol of strain in the least strained isomer of  $\text{Co}(\text{18N6})^{3+}$ . In addition, the isomerizations and racemizations observed, the structure of the  $\text{Co}(\text{21N6})^{3+}$  isomer isolated, the generally high reactivity, and the unusually high intensity and low energy of the  $T_{1g}$  bands in the absorption spectra<sup>27</sup> all suggest rather highly strained systems. However, the question of the mechanisms of the observed changes is of

(24) A structure of this type would give rise to the tetragonally compressed type of ESR spectrum for the analogous Ni(III) complex observed by Bencini, A.; Fabbri, L.; Poggi, A. *Inorg. Chem.* **1981**, *20*, 2544.  
(25) We wish to thank Professor Yoshikawa for kindly sending us a copy of the complete results of his conformational analysis calculations.

(26) Harnung, S. E.; Sorenson, B. S.; Creaser, I.; Maegaard, H.; Pfenninger, U.; Schaffer, C. E. *Inorg. Chem.* **1976**, *15*, 2123.  
(27) This shift to lower energy is just the reverse of the effect noted with the tetraaza macrocycles, where the bands are usually shifted to somewhat higher energies.

some interest, because of the very constrained nature of these complexes. The observed racemizations and  $D3 \rightleftharpoons D2$  isomerizations require rather drastic rearrangements. The conventional Bailar and Ray-Dutt twist mechanisms are not possible due to the interlinkage of the chelate rings, and mechanisms involving the breaking of a single bond also do not seem to be possible. Topologically, the simplest way to carry out the  $D3 \rightleftharpoons D2$  change seems to be interchanging the ends of a given chelate ring while simultaneously inverting the absolute configurations of both of the nitrogens. If this is actually what is occurring, it seems to require the simultaneous breaking of two adjacent cobalt-nitrogen bonds, which seems rather drastic, but no simpler process seems to be possible.

**Circular Dichroism.** It was originally anticipated that these complexes would be excellent systems for testing some of the theories of the origin of the optical activity in the d-d bands of transition-metal complexes. It was felt that the apparent conformational rigidity due to the linking of the chelate rings, the absence of any unsaturation, and the large number of ligand atoms in fixed chiral positions relatively close to the metal atom should make these complexes excellent systems for quantitative calculations on the basis of the dynamic coupling model of Mason and Seal<sup>6</sup> and the AICD model of Schipper.<sup>7</sup> This hope has been somewhat frustrated due partially to the inability to obtain more crystal data but, more importantly, to the nature of the complexes themselves. However, some qualitative conclusions can be drawn.

Calculations based on the dynamic coupling model, using crystal structure data when available and estimated values otherwise, rather consistently underestimated the observed rotational strengths of the  $T_{1g}$  bands by about 30–50%, and probably more significantly they seriously underestimated the increase in dipole strength of the band relative to that of  $\text{Co}(\text{NH}_3)_6^{3+}$ , the calculated dipole strength increase never being more than about 30% of the observed increase. These calculations are rather insensitive to moderate changes in the positions of any of the ligand atoms other than the ligating nitrogens, and so it is felt that the observed trend is probably not due to poor data. This result, together with the high observed dipole strengths  $((32-40) \times 10^{-38}$  cgsu as compared to typical tris(bidentate)cobalt(III) hexaammine complex values of  $(10-18) \times 10^{-38}$  cgsu) would seem to suggest that the large amount of steric strain in these complexes is distorting the coordination environment of the cobalt to the extent that there is a significant directly allowed electric dipole contribution to the d-d bands in the spectrum. Such a contribution is not readily incorporated into the calculations.

This distortion of the coordination environment also violates the postulates of the AICD model, and so the additive effect of additional chelate rings predicted by the simple form of that model would not be expected to hold.

However, there seems to be a reasonably good empirical correlation between chelate ring type and the sign and magnitude of the CD extremum ( $\epsilon_1 - \epsilon_2$ ) in the  $T_{1g}$  region:  $\Lambda\text{-Co}(\text{en})_3^{3+} +1.91$ ,  $\Lambda_5\Delta_6\text{-Co}(21\text{N}6)^{3+28} +1.40$ ,  $\Lambda\Lambda\text{-Co}(18\text{N}6)^{3+} +1.2$  and  $+1.0$ ;  $\Lambda(\text{ob})_3\text{-co}(\text{chxn})_3^{3+25} +4.45$ ,  $\Lambda_{\text{chxn}}(\text{ob})_3\Delta_{\text{en}}\text{-Co}(\text{TC}18\text{N}6)^{3+} +4.1$  and  $+4.2$ ;  $\Lambda(\text{lel})_3\text{-Co}(\text{chxn})_3^{3+25} -2.45$ ,  $\Lambda_{\text{chxn}}(\text{lel})_3\Delta_{\text{en}}\text{-Co}(\text{TC}18\text{N}6)^{3+} -2.8$  and  $-3.4$ .

If this trend is general, it would seem to imply that the observed CD spectrum is determined largely by the smallest and/or most rigid chelate rings present with the remaining chelate rings having only a minor effect. This is not unreasonable, because it is the small rigid chelate rings that would be expected to largely determine the conformation of the entire complex.

Schipper<sup>29</sup> has suggested that the weak circular dichroism in the magnetically forbidden bands (in this case the  $T_{2g}$  band at higher energy) might be useful in assigning absolute configurations. This suggestion does not seem to be useful in these cases, at least in the absence of polarization information. All six of the  $\text{Co}(\text{TC}18\text{N}6)^{3+}$  spectra, which must contain both  $\Delta\Delta$  and  $\Lambda\Lambda$  isomers, show positive rotatory strength in this band, while  $\Lambda_5\Delta_6\text{-Co}(21\text{N}6)^{3+}$  and  $\Lambda\Lambda\text{-Co}(18\text{N}6)^{3+}$  show negative strength in this band.

**Acknowledgment.** We wish to thank Peter J. Biltoft, who did much of the preparative work on  $\text{TC}18\text{N}6$ .

**Registry No.** *rac*- $\text{Co}(21\text{N}6)(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ , 80800-38-0; *rac*- $\text{Co}(18\text{N}6)(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ , 80844-85-5;  $\Lambda_5(\lambda\lambda\lambda)\Delta_6(\text{skew boat})_3\text{-Co}(21\text{N}6)^{3+}$ , 80844-86-6;  $\Lambda(\delta\delta\delta)\Lambda(\delta\lambda\lambda)m(1,2)\text{-Co}(18\text{N}6)^{3+}$ , 66289-55-2;  $\Lambda(\delta\delta\lambda)\Lambda(\delta\delta\lambda)m(1,4)\text{-Co}(18\text{N}6)^{3+}$ , 66289-56-3;  $\Delta_{\text{chxn}}(\lambda\lambda\lambda)\Delta_{\text{en}}(\delta\delta\delta)\text{-Co}(\text{TC}18\text{N}6)^{3+}$ , 80800-39-1;  $\Lambda_{\text{chxn}}(\lambda\lambda\lambda)\Delta_{\text{en}}(\lambda\lambda\lambda)\text{-Co}(\text{TC}18\text{N}6)^{3+}$ , 80875-76-9;  $\Delta_{\text{chxn}}(\lambda\lambda\lambda)\Delta_{\text{en}}(\delta\delta\lambda)m(S,S)\text{-Co}(\text{TC}18\text{N}6)^{3+}$ , 80875-77-0;  $\Delta_{\text{chxn}}(\lambda\lambda\lambda)\Delta_{\text{en}}(\delta\lambda\lambda)m(R,S)\text{-Co}(\text{TC}18\text{N}6)^{3+}$ , 80875-78-1;  $\Lambda_{\text{chxn}}(\lambda\lambda\lambda)\Delta_{\text{en}}(\delta\delta\lambda)m(S,S)\text{-Co}(\text{TC}18\text{N}6)^{3+}$ , 80875-79-2;  $\Lambda_{\text{chxn}}(\lambda\lambda\lambda)\Delta_{\text{en}}(\delta\lambda\lambda)m(R,S)\text{-Co}(\text{TC}18\text{N}6)^{3+}$ , 80844-87-7;  $\text{Co}(18\text{N}6)^{3+}$ ,  $D_{3d}$  isomer, 66251-24-9.

**Supplementary Material Available:** Listings of thermal parameters, hydrogen positions, and calculated and observed structure factors for the two structures (29 pages). Ordering information is given on any current masthead page.

(28) Perhaps a better comparison in this case would be with  $\text{ob-Co}(\text{pn})_3^{3+} +1.2$ , because the five-membered rings are ob in the macrocycle.

(29) Schipper, P. E. *J. Am. Chem. Soc.* **1979**, *101*, 6826.