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Isomeric Macrocyclic Tetramine Complexes of Cobalt(III). Some Problems of Stereochemistry and Chemical Reactivity[1]

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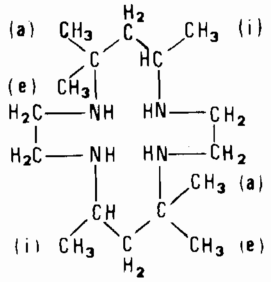
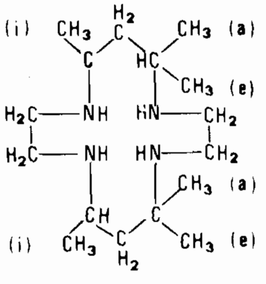
Cis-trans *and ligand configurational equilibria have been investigated in several* $Co^{III}(N_4)X_2$ *complexes, where* (N_4) *designates a Curtis-type macrocyclic tetramine ligand. Ligand configurational isomers are assumed to result from changes in the configuration of atoms around asymmetric coordinated nitrogen atoms. Several new isomers have been detected and tentatively assigned structures. Interconversion between isomers has been found to be relatively rapid in dilute acid. Several ligand configurations of* trans-$Co(N_4)(OH_2)_2^{3+}$ *appear to have about the same energy as the most stable* cis-*diaquo isomer, whereas* cis-$Co(N_4)Cl_2^+$ *has been shown to be far less stable than* trans-$Co(N_4)Cl_2^+$.

Introduction

We have been interested in the relationships between ligand stereochemistry and the reactivity patterns of coordination complexes. We have found that the methyl substituted, macrocyclic tetramines originally developed by Curtis,[2] provide particularly dramatic stereochemical alterations of normal reactivity patterns. For example, the acid hydrolysis of bidentate carbonate in Co(tet*b*)CO_3^{+3} proceeds at less than 10^{-4} the rate of hydrolysis of the Co(en)$_2$$CO_3^+$ analog.[4a]





In the course of extending our previous mechanistic studies,[4] we have prepared and characterized two isomerically different complexes of Co(tet*b*)CO_3^+. In addition, we have characterized the isomeric Co(tet*d*)CO_3^+ complex. Acid hydrolysis of each of these isomers produces a different *cis*-CoL$(OH_2)_2^{3+}$ complex. The detailed mechanistic studies of the reactions of these complexes have proved to be intricate and complicated and will be reported elsewhere. The present report is confined largely to our characterizations of these isomeric species and of the chemical relationships between them.

The stereochemistry of the nickel(II) complexes with these same macrocyclic tetramine ligands has been the subject of recent interest.[5-8] The assignment of isomers in these studies has reached a satisfactory state of agreement between various laboratories. The present report draws heavily from these previous studies. However, stereochemical interactions are different in cobalt(III) and nickel(II) complexes since the former are necessarily six coordinate while the latter may be four or five coordinate. Partly due to its higher coordination number and partly due to substitution inertness, stereochemical change is relatively slow (compared to nickel(II)) in cobalt(III) complexes. In fact, we have found some reaction pathways, and some isomeric species, in the cobalt(III) complexes which are as yet unreported for the nickel(II) analogs

Experimental Section

A. *Preparation of Macrocyclic Ligands.* The free tet*b* ligand was prepared according to literature procedures.[9] The presence of tet*a* impurity in the tet*b* sample is not considered likely since the separation procedure capitalizes on the relatively great ease with which the tet*b* ligands may fold to form "*cis*" complexes. A more serious possibility is contamination of tet*d* with tet*b* (or vice versa) since the preparation of these ligands requires a clean separation of [Ni(*trans*-[14]diene)]$(ClO_4)_2$ and [Ni(*cis*[14]diene)]$(ClO_4)_2$.

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[1] Partial support of this research by the Public Healt Service (Grant AM-143341) is gratefully acknowledged.

[2] For a review see N.F. Curtis, *Coord. Chem. Revs.*, 3, 3 (1968).

[3] The abbreviations used in this paper for macrocyclic ligands are: C-racemic-*trans*[14]tetramine (tet*b*) = C(5, 12) d, 1-5,7,7,12,14,14-hexamethyl-1,4,7,11-tetraazacyclotetradecane. C-meso-*cis*[14]tetramine (tet*d*) = C(5, 14) meso-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-*trans*[14]diene = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. *cis*[14]-diene = 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene cyclam = 1,4,8 11-tetraazacyclotetradecane.

[4] (a) J. A. Kernohan and J.F. Endicott, *J. Amer. Chem. Soc.*, *91*, 6977 (1969).
(b) *Inorg. Chem.*, *9*, 1504 (1970).

[5] L. G. Warner, Ph.D. Dissertation. Ohio State University.

[6] L. G. Warner and D. H. Busch, in «Coordination Chemistry», S. Krschner, ed, Plenum Press, New York, N. Y., 1969, p. 1.

[7] P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc.*, 1956 (1970).

[8] L. G. Warner and D. H. Busch, *J. Amer. Chem. Soc.*, *91*, 4092 (1969).

[9] P. O. Whimp and N. F. Curtis, *J. Chem. Soc.*, *A*, 867 (1966).

The [Ni(*cis*[14]diene)]$(ClO_4)_2$ complex is the first to crystallize out of the reaction mixture, [Ni(en)$_3$]$(ClO_4)_2$[10] in acetone, with the highest yields being obtained for condensation run in the dark at temperatures below ambient. A complete separation of *cis* and *trans*[14]diene complexes is difficult to obtain. In the present study several recrystallizations from H_2O of [Ni(*cis*[14]diene)]$(ClO_4)_2$ and a single recrystallization of [Ni(*trans*[14]diene)]$(ClO_4)_2$ were necessary. Infrared spectra offer the most critical test of purity of samples[11] although differences in pmr spectra are also very helpful.[12] Isomeric contamination is probably more likely in the case of the tet*d* ligand, since the yield of [Ni(*cis*[14]diene)]$(ClO_4)_2$ is only about 20-40% of the yield of the *trans*[14]diene isomer.

To assist with the pmr assignments selectively deuterated tet*b* was prepared. A 0.04 *M* NaOH solution in D_2O was prepared by dissolving 0.256 g NaOH in 160 ml 99.7% D_2O. To this solution was added [Ni(*trans*[14]diene)]$(ClO_4)_2$ (20.0 g). This solution was refluxed for 2.5 hrs. After refluxing, the solution was heated to 75°C on a hot plate, and 6.0 g $NaBH_4$ was added slowly with stirring over a 15 min period. A thick mauve product (borohydride adduct) precipitated from solution, and persisted even after constantly stirring at 70°C for 45 min. To avoid further loss of D_2O, this mauve precipitate was collected. A large excess of $NaClO_4$ was added to the filtrate, and an orange precipitate which formed (a mixture of deuterated [Ni(tet*a*)]$(ClO_4)_2$ and [Ni(tet-*b*]$(ClO_4)_2$) was filtrered.

The mauve and orange precipitates were combined and suspended in 500 ml of hot water. These solids dissolved after stirring the mixture near boiling for 15 min. The hot solution was filtered to remove a trace amount of black residue (presumably Ni metal). Solid sodium oxalate (9.0 g) was added, and the solution was heated near boiling for 20 min with occasional stirring. The blue precipitate of [Ni(tet*b*)]$_2$$(C_2O_4)(ClO_4)_2$ was filtered from the hot solution, and washed with 10 ml each of water, ethanol, and ether. Yield of [Ni(d_{12}-tet*b*)]$_2$$(C_2O_4)(ClO_4)_2$ = 6.0 g. The filtrate on standing several days in the refrigerator yielded 3.8 g of orange [Ni(d_{12}-tet*a*)]$(ClO_4)_2$ product.

The free d_{12}-tet*b* ligand was obtained from the blue oxalate dimer according to the procedure of Curtis.[9] The product was washed with 45 ml of cold water and air dried. Yield, 2.5 g. The filtrate and water washings (plus 2.7 g of calcium hydroxide) were evaporated to dryness on the rotary evaporator. The residue was extracted two times by refluxing with *n*-hexane (250 ml each extraction). This procedure[13] yielded a further 1.5 g of free tet*b*. The first precipitate was recrystallized from 20 ml hot 50% ethanol, and 1.8 g of product was obtained after washing with 10 ml cold water and drying. Infrared spectra of this recrystallized fraction of the tet*b* ligand indicates that reduction was complete (no C=N stretch at 1660 cm^{-1}) and that deuteration was successful (intense C–D hands at 2120 and 2220 cm^{-1}).

B. *Preparation of Complexes.* Literature procedures[14] were used to prepare *trans*-[Co(tet*b*)Cl_2]ClO_4. Several attempts to prepare *trans*-[Co(tet*b*)$(OH_2)_2$]$(ClO_4)_3$ by air oxidation of solutions of $Co(ClO_4)_2 \cdot 6H_2O$ and the free ligand failed to yield identifiable products.

1. [Co(tet*b*)(CO_3)]ClO_4 (isomers α and β). Two alternate routes have been used for the preparation of these carbonate complexes: (1) the addition of Na_2CO_3 to a basic solution of *trans*-[(tet*b*)Cl_2]ClO_4 and (2) the addition of free ligand (tet*b*) to a hot aqueous solution of $Na_3[Co(CO_3)_3]$.[15]

Method I: 5 ml conc. NH_4OH was diluted to 30 ml and the solution added to *trans*-[Co(tet*b*)Cl_2]ClO_4 (1.00 g). The solution was heated 5 min on a hot plate and filtered hot. Solid $Na_2CO_3 \cdot H_2O$ (0.30 g) was then added, and the solution heated for 5 min. The purple product began to precipitate after about 2 min heating. The solution was cooled in an ice bath and the product was isolated and washed. Yield 0.50 g. Calcd for $CoC_{17}H_{37}N_4O_{7.5}Cl$: C, 39.9%; H, 7.3%; N, 10.9%; Cl, 6.9%. Found: C, 39.1%; H, 7.1%; N, 10.7%; Cl, 7.2%.

Various fractions from this preparation and from the recrystallization procedures had identical infrared and visible spectra, and acid hydrolysis led to the pmr spectrum characteristic of a single isomer of *cis*-Co(tet*b*)$(OH_2)_2^{3+}$ (Figure 1). This is the isomer designated "isomer α" below. As noted, the yield (based on Co(tet*b*)Cl_2^+ of isomer α runs around 50%. Additional carbonate complexes may be precipitated by concentrating the supernatant solution and adding more $NaClO_4$. This soluble isomer of [Co(tet*b*)CO_3]ClO_4 has been designated "isomer β". In most of our work the β isomer was prepared by Method II.

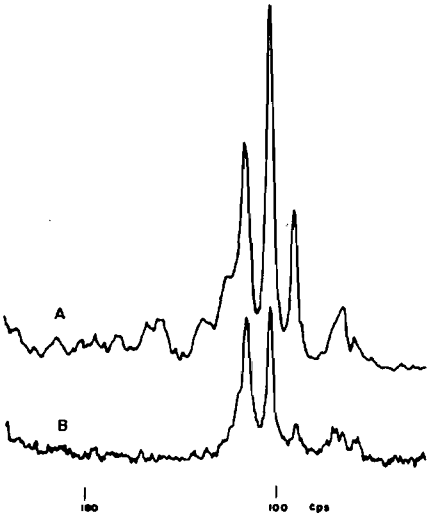

Figure 1. Methyl region pmr spectra of α-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$ A; and α-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$, B, selectively deuterated at the C-5 and C-12 methyl groups.

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[10] N. F. Curtis, *ibid.*, *C*, 1979 (1967).
[11] P. O. Whimp and N. F. Curtis, *ibid.*, *A*, 1827 (1966).
[12] L. G. Warner, N. J. Rose, and D.H. Busch, *J. Amer. Chem. Soc.*, *90*, 6939 (1968).
[13] N. F. Curtis, *ibid.*, 2644 (1964).
[14] (a) P. O. Whimp and N. F. Curtis, *ibid.*, *A*, 86 (1966); (b) *ibid.*, *A*, 188 (1968).
[15] H. F. Bauer and W. C. Drinkard, *J. Amer. Chem. Soc.*, *82*, 5031 (1961).

Method II. To a suspension of 1.0 g purified tet*b* in 20 ml hot water, were added 1.2 g freshly prepared $Na_3[Co(CO_3)_3]$. The reaction mixture was heated with stirring on a hot plate for 10 min and filtered hot. The solution was heated an additional 20 min, during which time much of the purple product precipitated. The pH was adjusted to approximately 8 with $HClO_4$, and the solution cooled in an ice bath. The product was collected and washed with 50% ethanol, anhydrous ethanol, then ether. Yield 0.84 g. $NaClO_4$ was added to the filtrate to obtain additional product. Yield of ppt. B, 0.15 g. The diaquo complexes obtained from and hydrolysis of these preparative fractions had complex pmr spectra indicative of more than one isomeric species. To purify these materials the combined precipitates (0.95 g) were added to 45 ml water, and the mixture heated near boiling for 5 min. A large amount of material remained undissolved and was removed by filtering the hot solution. The purple product (powder) was washed and found to be indistinguishable from isomer α. When the filtrate from this recrystallization was cooled in an ice bath, a second crystal fraction was obtained. Addition of $NaClO_4$ resulted in precipitation of a third fraction. The combined yield of second and third fractions was 0.25 g. These crystal fractions gave acid hydrolysis products with a new and complex pmr spectrum (Figure 2). Calcd for $CoC_{17}H_{37}N_4O_{7.5}Cl$: C, 39.9; H, 7.3; N, 10.9; Cl, 6.9. Found: C, 39.4; H, 7.0; N, 10.5; Cl, 5.9.

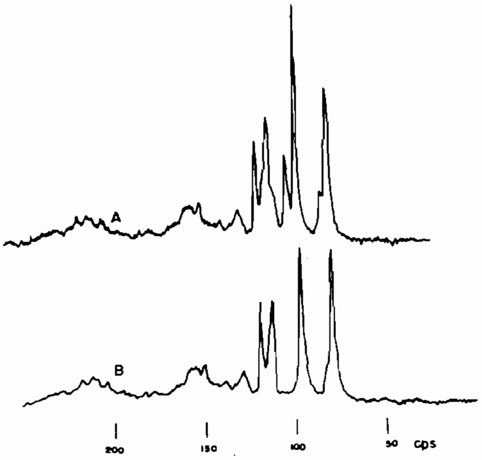

Figure 2. Methyl region pmr spectra of β-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$. A is the observed spectrum; B is a corrected spectrum assuming some α-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$ was present in the sample.

[Co(d_{12}-tet*b*)CO_3]ClO_4 (isomer α). The d_{12}-tet*b* ligand (deuterated at the C-5 and C-12 methyl and hydrogen atoms and at the bridging methylenes. C-6 and C-13)[3] was used in a variation of Method II to prepare this complex. The yield of isomer 3 was too small in this preparation to permit purification.

2. [Co(tet*d*)CO_3]ClO_4. In a procedure analogous to that used for the tet*b* complexes, 1.5 g tet*d* was suspended in 35 ml hot water and freshly prepared $Na_3[Co(CO_3)_3]$ 91.5 g was added. The reaction mixture was heated for 5 min on a hot plate, with stirring, then filtered hot. A few drops of conc. $HClO_4$ were added to adjust the pH to about 10 and the solution was cooled to room temperature. A deep purple crystalline product was collected and washed with 10 ml each of cold water, ethanol, then ether. Yield 0.69 g. Calcd for $CoC_{17}H_{37}N_4O_{7.5}Cl$: C, 39.9; H, 7.3; N, 10.9; Cl, 6.9. Found: C, 40.0; H, 7.5; N, 10.7; Cl, 7.1.

A second crystal fraction could be obtained by adding $NaClO_4$ to the filtrate from the above preparation. This second crystal fraction was relatively light in color and had elemental analyses visible and pmr spectra consistent with a mixture of the free tet*d* . 2-$HClO_4$ ligand (70-80% by weight) and the isomer separated in the first fraction. No additional isomeric [Co(tet*d*)CO_3]ClO_4 species could be separated from this or other preparative methods atetempted.

C. *Pmr Spectra.* Most pmr spectra reported here were recorded on a Varian T60 at ambient temperatures (~35°). In many cases, these same spectra were measured on a Varian A60 instrument; the two sets of spectra were identical. All spectra are reported for the region 0-250 cps. For the spectra in D_2O, it was not feasible to determine the chemical shifts relative to internal TMS. In addition, water soluble sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was not successful as an internal reference in these cases, since its addition resulted in the precipitation of a complex species. The relative chemical shifts were therefore obtained by the following procedure: Kernohan and Endicott[4a] report the pmr of *trans*-Co(*trans*[14]diene)$(OH_2)_2^{3+}$ in $HClO_4/D_2O$, the chemical shifts being relative to external TMS. This spectrum was used as the standard in the present work. Thus, for example, the chemical shifts for *cis*-Co(tet*b*)-$(OH_2)_2^{3+}$ (isomer β) were obtained from the pmr spectrum of a 1:1 mixture of *trans*-Co(*trans*[14]diene)-$(OH_2)_2^{3+}$ and *cis*-Co(tet*b*)$(OH_2)_2^{3+}$ (isomer β) in $HClO_4/D_2O$.

In $NaOH/D_2O$ solution no such suitable standard was available. However, these spectra were normally run in between acid solution spectra. Favorable conditions were occasionally obtained where very little field fluctuation was observed between two such acid solution spectra. In these cases, the chemical shifts of the NaOH solution could be related to the standardized shifts in the two acid solutions. All NaOH solution spectra were then calibrated by appropriate solution mixing. Although this procedure may have resulted in small errors in the absolute chemical shifts ,the NaOH spectra are accurately related to each other.

Similarly, for $HClO_4/D_2O$ solutions containing NaCl, *trans*-Co(*trans*[14]diene)$(OH_2)_2^{3+}$ anates and cannot be used as a standard. In these cases, the same procedure adopted for the NaOH solutions was used.

Results

A. *Physical Characterization of Isomeric Species.*

1. Isomers of [Co(tet*b*)CO_3]ClO_4. These isomers may be distinguished by their infrared and visible

(Figure 3) spectra. A more sensitive distinction may be made using the acid hydrolysis products as noted below.

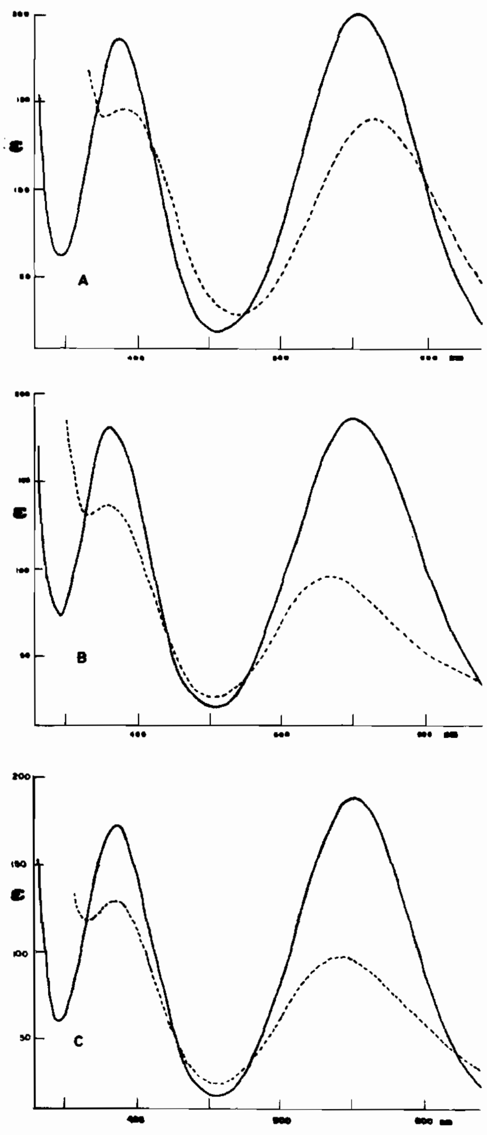

Figure 3. Visible absorption of $CoLCO_3^+$ (solid line) and *cis*-$CoL(OH_2)_2^{3+}$ (dashed line) complexes. A, α-*cis*-Co(tet*b*)X_2; B, β-*cis*-Co(tet*b*)X_2; C, α-*cis*-Co(tet*d*)X_2.

The visible spectra of isomers α and β are compared in Figure 3. The observed difference in extinction coefficients (~8%) of the two isomers at their first d–d absorption maximum is outside experimental error, and is considered real (isomer α, 554 nm (ε = 200); isomer β, 551 nm (ε = 184)). It was of interest to see if both isomers would equilibrate on standing in aqueous solution over prolonged periods. The absorbance at 550 nm of an isomer α solution increased by 2.5% on standing at room temperature for 5 months, while that of isomer β decreased by 2% over a 6-month period. Absorbance changes in other regions of the spectrum were insignificant. Both the changes observed are in the opposite direction to that expected for equilibration, and are attributed to experimental error. It is also noted that these complexes may be recrystallized from water without isomeric scrambling.

2. Isomers of Co(tet*b*)$(OH_2)_2^{3+}$. The diaquo species were obtained from the carbonato complexes as follows: several drops of conc. $HClO_4$ (10-12 *M*) were added to the solid carbonato complexes. Rapid evolution of CO_2 was observed, and the solution was swirled until all solids dissolved (<1 minute). The solution was diluted with distilled water to the required acidity. Solid samples were not always isolated in the present work, although they have been obtained when a large quantity of carbonato complex was used.

The visible spectra of the diaquo complexes in 2.2 *M* $HClO_4$ are compared with those of their respective carbonato parents in water solution in Figure 3. Large spectral differences are apparent in Figure 3, both in the position of the first d–d absorption maximum and in its extinction coefficient (isomer α, λ_{max} 565 nm, ε = 149; isomerβ, λ_{max} 534 nm, ε = 95). Both isomers are assigned the *cis*-configuration on the basis of these relatively high extinction coefficients. By way of comparison, *cis*-Co(cyclam)$(OH_2)_2^{3+}$ has been reported to have its first *d–d* band at 506 nm with ε = 110.[16,17]

The most prominent and useful features of the pmr spectra of the *cis-Co*(tet*b*)$(OH_2)_2^{3+}$ complexes are the resonances in the methyl region (Figures 1 and 2). For *cis*-Co(tet*b*)$(OH_2)_2^{3+}$ (isomer α) methyl resonances are observed with approximate intensity ratios of 1.0:1.5:0.5 at 95.7, 101.8, and 108.4 cps, respectively. The deuteration of the imine methyl groups of Ni(*trans*[14]diene)$^{2+}$ before reduction of the ligand leads to *cis*-Co(d_{12}-tet*b*)$(OH_2)_2^{3+}$ complexes in which the only observed methyl resonances are of equal intensity at 95.7 and 101.8 cps.

The pmr spectrum of *cis*-Co(tet*b*)$(OH_2)_2^{3+}$ (isomer β) is complex (Figure 2) even in the methyl region. This spectrum exhibits peaks at 96.8 and 101.8 cps have not succeeded in changing the relative intensities of the methyl resonances in our recrystallization procedures; however, the isomeric separations are sufficiently difficult that possibility of such a large (10-20 percent) contamination by isomer α cannot be eliminated. We have therefore included in Figure 2 a "corrected" spectrum from which we have subtracted an isomer α spectrum, attributing the 101.8 cps resonance entirely to the latter complex.

3. Co(tet*d*)$(CO_3$ and *cis*-Co(tet*d*)$(OH_2)_2^{3+}$. Visible absorption spectra of these complexes have been included in Figure 3; a summary of the methyl region pmr spectrum is found in Table I.

B. *Chemical Relationships and Transformations of Co^{III}(tet*b*)X_2 Isomers.*

1. Acidic Solutions. In acid solution the Co(tet*b*)-CO_3^+ and *cis*-Co(tet*b*)$(OH_2)_2^{3+}$ complexes were found to be readily transformed into *trans*-Co(tet*b*)Cl_2^+ for

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(16) C. K. Poon and M. L. Tobe, *J. Chem. Soc., A*, 1549 (1968).
(17) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, *4*, 1102 (1965).

Table I. Estimated Assignments of Methyl Pmr Chemical Shifts[a] of $CoL(OH_2)_2^{3+}$ Isomers.

Isomer	CH_3(i)	CH_3(e)[b]	CH_3(e)[b]
A . L = tet*b*			
α-cis	108, 102[c]	102	96
β-cis	119, 112[d]	97[d]	80[d]
α-trans	(139, 133)[f]	(127)[f]	(119)[f]
β-trans	(97, 80)[f]	(104)[f]	(99)[f]
γ-trans[e]	119, 113[c]	96	84
δ-trans-[e]	114, (?)	(?)	79
ω-trans[g]	119, 114, 109[c]	114	88, 83
B . L = tet*d*			
α-cis[h]	113, 107, 101, 95	113, 101	95, 83
β-trans[g]	118, 112, (?)	117	93, 88, (?)
γ-trans	113, 107	113	83

[a] In cps. See text for reference basis. [b] There is no unequivocal basis for assigning the resonances due to axial and equitorial geminal methyl groups. Examination of our data and molecular models suggests that the induced magnetic fields have a complex geometry so that the local field experienced by a methyl group depends on how it is positioned with respect to the bonding axes at the metal center. [c] CH_3(i) resonances disappear in deuterated complex. [d] This assignment assumes that the β-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$ sample was contaminated with 10-20% of the α-isomer. [e] Intermediate species in isomeric interconversions; Schemes I and II, Figures 4 and 5. [f] Chemicals shifts for Co(tet*b*)Cl_2^+; external TMS reference. [g] Immediate product when base equilibrated isomers are acidified. May not be isomerically pure. [h] Approximate ratio of peak intensities is 1.5:0.5:1.5:1.5:1.0 for peaks at 113, 107, 101, 95, and 83 cps, respectively. The differences in chemical shifts of pairs of peaks at about 101 and 107 cps, 83 and 101 cps, and 107 and 113 cps in 60 Mc spectra increased about 50% in 100 Mc spectra. Some resolutions of the components of the 107 cps peak (60 Mc spectrum) were obtained at 100 Mc.

both the α and β series of isomers. These *trans* isomers differed in their solubility in water (the α isomer being more soluble), in their color and pmr spectra (Table I). The same isomer of *trans*-Co(tet*b*)Cl_2^+ was obtained from Co(tet*b*)CO_3^+ or from *cis*-Co(tet*b*)$(OH_2)_2^{3+}$. We have investigated the α series of isomers most carefully. Treatment of α-*trans*-Co(tet*b*)Cl_2^+ with $AgClO_4$($[HClO_4] \geqslant 10^{-3}$ *M*) resulted in the immediate formation of a purple solution which appeared to contain α-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$ in addition to several other isomers (see Figure 4). In the experiment shown in Figure 4, $[D^+] = 0.1$ *M*, a condition favoring the slow decomposition of the complex (see below), a precipitate formed after several days. This precipitate was a mixture of predominately colorless crystals (probably tet*b* . $2HClO_4$) mixed with a few deep red crystals. It is to be noted that after standing five days, a solution prepared from the solid [α-*cis*-Co(tet*b*)$(OH_2)_2$]$(ClO_4)_3$ in 0.25 *M* $DClO_4$(D_2O exhibited a pmr very similar to that in Figure 4a. It is further to be noted that tet*b* dissolved in 0.1 *M* $DClO_4$ exhibits an intense pmr band at about 104 cps. These complexities and the difficulty in preparing isomerically pure complexes makes the assignment of methyl resonances ambiguous for the various Co(tet*b*)$(OH_2)_2^{3+}$ complexes. Despite these unavoidable ambiguities, it is clear that the isomeric diaquo complexes are numerous and interconvert relatively easily even in acidic solution. It also appears that there are at least three complexes of roughly comparable stability which co-exist at comparable concentrations after several days in 0.1-0.25 *M* H^+, regardless of the manner of preparation of the original solution (see also 2 below). We have tentatively identified these complexes as α-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$, γ-*trans*-Co(tet*b*)$(OH_2)_2^{3-}$, and δ-*trans*-Co(tet*b*)$(OH_2)_2^{3-}$. It is important to note that the isomer assigned as δ-*trans*-Co(tet*b*)$(OH_2)_2^{3+}$ was observed to continue to increase in concentration over a period of several days in solutions prepared from either α-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$ or α-*trans*-Co(tet*b*)Cl_2^+. In Table I we have made some tentative assignments of pmr bands in the methyl region,[18] but our assignments are certain only for the α- and δ-*cis*-CoL$(OH_2)_2^{3-}$ and the α- and β-*trans*-CoLCl_2^+ complexes.

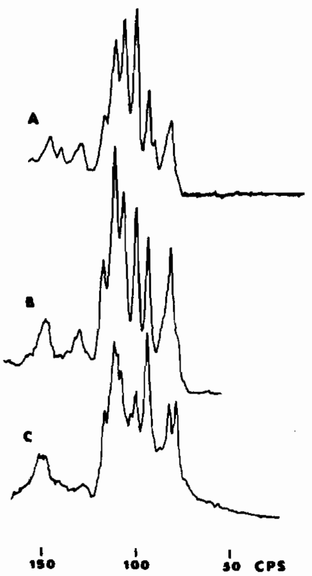
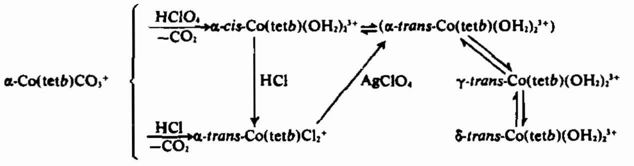


Figure 4. Methyl region pmr spectra of isomerizing Co(tet*b*)$(OH_2)_2^{3+}$ complexes prepared from α-*trans*-Co(tet*b*)Cl_2^+. A, initial spectrum following separation of AgCl; B, solution after 12 hrs; C, solution after 8 days. Some material had precipitated in the final solution (see text).



Scheme 1

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(18) In this paper we use « equitorial » as a designation for groups which are directed away from faces and edges of an ectahedron centered at the cobalt and "axial" as a designation for groups which lie in or near such an octahedral face or edge.

The reactions of the α-isomers in acidic solution may be summarized as in Scheme 1.

The *cis*-Co(tet*b*)$(OH_2)_2^{3-}$ complexes are not thermally stable in acidic solution. This instability is evidenced by changes in the visible absorption spectrum in addition to pmr spectral changes discussed above. These reactions are retarded by acid and may therefore be regarded as involving inversion of configuration around the asymmetric nitrogens.

Isomer α was found to be considerably more labile than isomer β. For the first five hours of reaction in 2.2 *M* $HClO_4$ at 25° three isosbestic points at 377, 441, and 487 nm were observed, consistent with a single reaction pathway. During this time the wavelength of the first d–d absorption maximum remained constant. Over longer periods of time, the isosbestic points were destroyed, and the absorption maximum shifted to shorter wavelengths. In 0.25 *M* $HClO_4$ solution at 25°C no isosbestic points were evident, and an immediate shift in the absorption maximum to shorter wavelengths was observed. The spectrum of the final "equilibrium" product at 25°C is not know with certainty.

Spectral changes for isomer β in acid solution are quite slow at 25°C. In 2.2*M* $HC1O_4$, no isosbestic points were observed, the absorbance decreasing over the entire wavelength range studied (370-700 nm.). The visible absorption maximum initially moved to shorter wavelengths, but on prolonged standing a shift to higher wavelenghts was observed. Although the final equilibrium spectra at 25°C are uncertain, it seems likely that isomers α and β yield similar product solutions having absorption maxima in the region 545-560 nm.

At higher temperatures (> 75°) acid solutions of isomers α and β undergo complex transformations and decomposition. A complete analysis of this high temperature behavior has been frustrated by the complexities involved. However, our evidence suggests the same general reaction sequence for both isomers, and a common final reaction product. Spectral examination of the initial stage of reaction suggests that a common intermediate was produced by both isomers. Thus, for isomer α the wavelength of the first d-d absorption maximum decreased from 565-550 nm, while that of isomer β increased from 535 to ∾550 nm. For both isomers, pseudo isosbestic points were observed, but their positions shifted steadily with time indicating the reaction was not a simple one. Throughout these reactions there was a progressive increase in absorbance at 450 nm. This yellow reaction product eluted from a cation exchange resin as a +2 or +3 ion. Effluent fractions containing this species were bleached by treatment with base and did not appear to contain any cobalt complexes. The yellow solutions prepared by heating α- or β-*cis*-Co(tet*b*)-$(OH_2)_2^{3-}$ at 100° for 15-60 min exhibited very simple pmr spectra which indicated equivalence of all methyl groups; very similar to pmr spectra observed for the tet*b* ligand in acidic solution. These latter solutions have been found to contain Co^{2+}.

As noted above, the high temperature decomposition reaction proceeds in two stages at 80°. The first stage for isomer α had an apparent first order rate constant of approximately 3.5×10^{-4} sec^{-1} with an activation energy of about 31 kcal/mole. The second stage proceeded at similar rates (k_{obs} = $(2.4 \pm 0.1) \times 10^{-4}$ sec^{-1} at 80°) for both complexes and had a similarly high activation energy ($S_a \cong 31 \pm 1$ kcal/mole).

It is noteworthy that the form of the final reaction spectrum was found to be temperature dependent. Thus, although a shoulder at ~450 nm develops with time at 75°, it was not as intense or as well-resolved as in the reaction spectrum at 80°. On the other hand, when a 0.25 *M* $HClO_4$ solution of isomer α or β was heated near boiling for ~ 15 min, a yellow-amber solution resulted which had a very intense peak at 450 nm.

2. Basic Solutions. Solutions of α- and β-*cis*-Co-(tet*b*)$(OH_2)_2^{3+}$ made 0.3 *M* in NaOH and allowed to stand for 30 min (at room temperature or 65°) were indistinguishable in their visible absorption and pmr spectra. Thus it appears that some sort of isomeric equilibrium is relatively easily achieved in basic solutions. However, the pmr spectra are complex and suggest that either several species are present or that the six-membered chelate rings have very different conformations so that the methyl groups are no longer pair-wise matched. For simplicity in discussion we have adopted the latter hypothesis and will henceforth refer to this "species" as isomer ω.

Acidification of these base equilibrated solutions produced green solutions (λ_{max} = 585 nm, ε = 48) whose absorptivity was the same for solutions prepared originally from either α- or β-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$. In acid solution the ω isomer (or mixture of isomers) was not stable and changes were observed in both the visible absorption and pmr spectra over periods of several days. There are two qualitatively distinct reaction stages (observed both at 25° and 65°): in the first the solutions gradually (about one day at 25°)

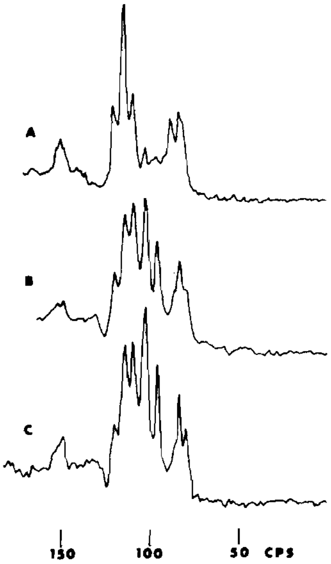


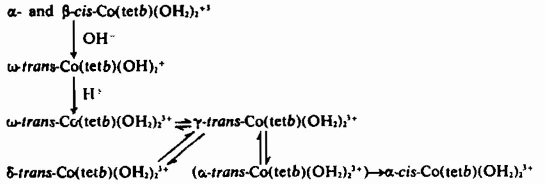
Figure 5. Methyl region pmr spectra of isomerizing Co-(tet)*b*)$(OH_2)_2^{3+}$ complexes prepared by treating α-*cis*-Co-(tet*b*)$(OH_2)_2^{3+}$ with NaOD then conc. $DClO_4$. A, spectrum a few min after acidification; B, spectrum after 4 days; C, spectrum after 10 days.

became purple (λ_{mxx} = 565 nm, $\varepsilon \geqslant 60$); in the second stage absorptivity decreased at wavelengths greater than 460 nm, while a shoulder appeared at 450 nm. This second stage was not observed or was greatly suppresesd for $[H^+] \geqslant 1$ *M*.

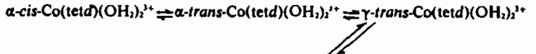
The pmr spectra in Figure 5 correspond to isomer changes in the first stage of reaction noted above. These spectra may be contrasted with those of the isomerization of α-*trans*-Co(tet*b*)$(OH_2)_2^{3+}$ in Figure 4. Although isomer distributions appear to differ, the pmr spectra of reaction mixtures of α- and ω-*trans* Co(tet*b*)$(OH_2)_2^{3+}$ (Figures 4 and 5) exhibit the same principle peaks. It seems evidente that most of the species generated are the same in each case; *i.e.*, we find evidence for γ- and δ-*trans*-Co(tet*b*)$(OH_2)_2^{3+}$ and α-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$ in each case in addition to the initial ω-*trans*-Co(tet*b*)$(OH_2)_2^{3+}$. Scheme II summarizes the simplest analysis of the isomerization of ω-*trans*-Co(tet*b*)$(OH_2)_2^{3+}$ which we have been able to make. Tentatively assigned chemical shifts for the methyl resonances of these various isomers have been collected in Table I.

C. *Chemical Relationships and Transformations of Co^{III}(tet*d*)X_2 Isomers.*

The one isomerically pure complex, α-*cis*-Co(tet*d*)$(OH_2)_2^{3+}$, which we have been able to prepare exhibited acid decomposition reactions very similar to those commented on in detail for the *cis*-Co(tet*b*)$(OH_2)_2^{3+}$ isomers. A series of reactions followed the treatment of *cis*-Co(tet*d*)$(OH_2)_2^{3+}$ with base which were very similar to those observed for *cis*-Co(tet*b*)$(OH_2)_2^{3+}$ in base. However, in the present case *cis*-CoL$(OH_2)_2^{3+}$ starting material was regenerated more cleanly and rapidly on acidification of the base "equilibrated" solutions (Figure 6). Furthermore, the pmr peaks of α-*cis*-Co(tet*d*)$(OH_2)_2^{3+}$ may be identified in initial acidic solution (spectrum B, Figure 6) suggesting that α-*cis*-Co(tet*d*)$(OH)_2^+$ was present in solution even after 30 min in base. In addition to the α-*cis* isomer there is evidence in the spectra in Figure 6 for at least two additional isomers. Since the initially acidified solutions are green and otherwise appear to be *trans*- complexes, we designated these additional isomers as β- and γ-*trans*-Co(tet*d*)$(OH_2)_2^{3+}$. These observations are summarized in Scheme III. We have included an α-*trans*- isomer in the reaction sequence in Scheme III even though this may be the same as the isomer identified as γ. As noted in the Discussion Section, it is doubtful that the α-*trans*-Co(tet*d*)$(OH_2)_2^{3+}$, necessarily present as a reaction intermediate, could easily achieve detectable levels of concentration under these conditions.



Scheme 2



Scheme 3.

Figure 6. Methyl region pmr spectra of some Co^{III}(tet*d*)X_2 species. A, spectrum of dihydroxy complex (in NaOD) prepared from α-*cis*-Co(tet*d*)$(OH_2)_2^{3+}$; B, some solution following acidification with conc. $DClO_4$; C, spectrum of acidified solution 10 days later; D, spectrum of α-*cis*-Co(tet*d*)$(OH_2)_2^{3+}$.

Chemical Inter-Relationships Among Isomers and General Discussion

A. *Isomeric Species in the* (*tet*b)*cobalt*(*III*) *Systems.*

Of the dozen or so possible Co^{III}(tet*b*)X_2 isomers, many clearly exist. In the case of the diaquo complexes interconversion of configurational isomers is apparently quite facile even in moderately strong acid. The most easily characterized of these species is α-Co(tet*b*)$(CO_3)^+$. This species will therefore be taken as a point of departure for our further discussion.

Treatment of α-Co(tet*b*)CO_3^+ with conc. $HClO_4$ leads to a single *cis*-diaquo isomer while treatment with conc. HCl leads to a single *trans*-isomer. If we assume that inversion about the nitrogens is slow in 10-12 *M* acid,[19]

$$\alpha\text{-Co(tet}b\text{)CO}_3^+ \begin{cases} \xrightarrow{HClO_4} \alpha\text{-}cis\text{-Co(tet}b\text{)(OH}_2)_2^{3+} \\ \xrightarrow{\qquad} \alpha\text{-}trans\text{-Co(tet}b\text{)Cl}_2^+ \end{cases}$$

then both products may be referred to as α-isomers and must have the same basic ligand stereochemistry. Equilibration of either α- or β-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$ in basic solution, followed by acidification eventually

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[19] Note that the *trans*-configurational isomers differ only in the configuration of atoms around the four ligating nitrogens.[7] Each inversion of configuration about a nitrogen atom, the process leading from one isomer to another, is presumably preceeded by and slower than dissociation of the amine proton. The pmr bands of amine protons in the diaquo complexes can only be observed in non-aqueous solvents or in solutions of extremely high acidity.

results in the formation of α-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$. Thus, we may infer that α-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$ is more stable than β-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$. These observations are reminiscent of the behavior and stability of α-Ni(tet*b*)$^{2+}$, and therefore we conclude that the macrocyclic ligand has the same fundamental stereochemistry (see Figure 7) in both the nickel(II) and cobalt(III) complexes. Since the relative chemical shifts of geminal and doublet methyl pmr bands are small and not easily correlated to the complex structure,[20] we have no strong positive evidence regarding the structure of β-Co(tet*b*)CO_3^+; however, it is clear that α-*trans*-Co(tet*b*)Cl_2^+ and β-*trans*-Co(tet*b*)Cl_2 are different isomers. The pmr spectra of various α and β isomers do show that the geminal and doublet methyl groups are paired, suggesting similar conformations of the two six-membered chelate rings of each complex. This is consistent with the predictions of Whimp, *et. al.*, that the second most stable folded ligand isomer would have basic ligand stereochemistry (VfEE).[21] We tentatively attribute this stereochemistry to the β isomers.

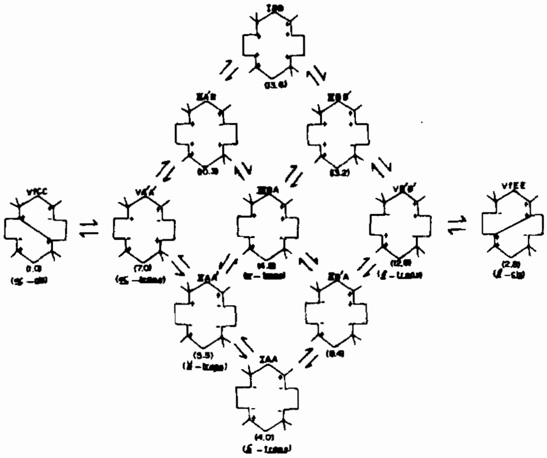
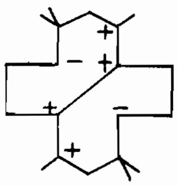


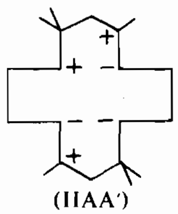
Figure 7. Stepwise isomerization scheme for the net conversion β-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$→α*cis*-Co(tet*b*)$(OH_2)_2^{3+}$. Probable configurations of isomers found in this study are indicated. Numbers in parenthesis are relative ligand conformational energies (in kcal/mole) as estimated in ref. 7. A «+» sign indicates an upward sense of the adjacent proton, a «—» sign a downward sense. Isomers are designated as in ref. 7.



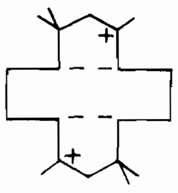
(VfEE)

Given the above assignments, i.e., that $^+$-*cis*-Co(tet*b*)-$(OH_2)_2^{3+}$ and β-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$ correspond to the configurational isomers of lowest predicted energy,[7] then it is possible to analyze our observations in terms of the stepwise configurational changes which may occur in these complexes. Thus, on the assumption that any isomerization such as β-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$ → α-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$ must proceed stepwise through *successive intermediates* which differ only through the inversion of configuration of groups about *one* nitrogen atom, all possible isomerization paths can be mapped out as in Figure 7. From Figure 7 it is seen that the isomerization β-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$→ α-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$ requires a minimum of six individual steps involving at least five intermediate isomeric complexes. We have found evidence for three or possibly four of these intermediate isomers.

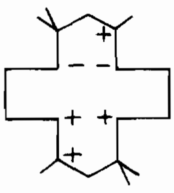
The calculations of the energetics of chelate ring conformations in four coordinate complexes as reported by Whimp, *et. al.*[7] are certain to be in error in the six coordinate cobalt(III) complexes. That the fifth and sixth ligands are very important in determining net isomeric stability is demonstrated by our observation that the Co(tet*b*)$(OH_2)_2^{3+}$ complexes readily assume a *cis*-geometry while all the Co^{III}(tet*b*)X_2^+ complexes tend to be *trans*. However, the relative energetics of the chelate ring conformations do provide useful insight into the behavior of the various *trans*-Co^{III}(tetb)X_2 complexes which we have observed. For example, α-*trans*-Co(tet*b*)$(OH_2)_2^{3+}$ is expected to be very unstable with respect to the lower energy chelate ring conformations of α-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$ and γ-*trans*-Co(tet*b*)$(OH_2)_2^{3+}$; in fact, structure (II AA′) is the only structure for the γ-isomer which is consistent with stepwise configurational changes and macrocyclic ligand conformational energetics. Furthermore, ligand configurations (IAA), (IIAA′), and (IIIBA) would all be expected to be similar in energy and closely related through stepwise transformations (Figure 7). Thus, we would associate our intermediate δ- and ω-*trans*-Co(tet*b*)$(OH_2)_2^{3+}$ isomers with structures (IAA) and (IIIBA), respectively. Since it appears that δ-*trans*-Co(tet*b*)$(OH_2)_2^{3+}$ grows out of ω-*trans*-Co(tet*b*)$(OH_2)_2^{3+}$ in each of Schemes I and II, we associate the δ-isomer with the "lowest energy"



(IIAA′)



(IAA)



(IIIBA)

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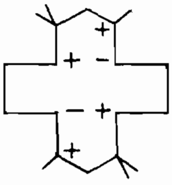
(20) (a) R. E. Ball, J. A. Kernohan, and J. F. Endicott, in "Coordination Chemistry", M. Cais, ed, Elsevier Publishing Co., Amsterdam, 1968, p. 117. (b) J. A. Kernohan, Ph. D. Dissertation. Boston University, 1968.

(21) Notation is that of ref. 7. Roman Numeral indicates basic cyclic stereochemistry; "f" that the ligand is folded along the axis indicated; capital letters indicate conformation of the six-membered chelate rings.

structure (IAA). Assignment of structure (IIIBA) to ω-*trans*-Co(tet*b*)$(OH_2)_2^{3+}$ is consistent (assuming that this a single isomeric species) with the pmr spectrum of this complex since the methyl groups in this stereoisomer cannot easily achieve similar chemical environments and the pmr spectrum indicates that only two of the methyl groups are paired.

The observation that the relative stabilities calculated for the various ligand configurations are consistent with our chemical observations in the Co(tet*b*)$(OH_2)_2^{3+}$ complexes, but not in the Co^{III}(tet*b*)X_2^+ complexes, suggests that some largely electrostatic factors (*e.g.*, X^-—X^- repulsion, solvation, etc«) are important enough to alter the balance of relative stabilities.

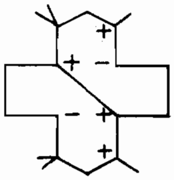
It is also to be observed that we have no evidence for α-*trans*-Co(tet*b*)$(OH_2)_2^{3+}$ even at moderately high $[H^+]$, even though this complex is a necessary intermediate in the configurational isomerization reactions. This is consistent with the predicted relatively high conformational energy for the (VA′A′) configuration.



(VA′A′)

B. *Isomeric Species in the* (tet*d*)*Cobalt*(*III*)*Systems.*

We have found the general patterns and many details of the chemistry of the Co^{III}(tet*b*)X_2 and Co^{III}(tet*d*)X_2 complexes to be very similar. One clear and predicted[7] difference is the relative stability of one *cis*-Co(tet*d*)$(OH_2)_2^{3+}$ complex compared to two *cis*-Co(tet*b*)$(OH_2)_2^{3+}$ complexes. Thus the α-*cis*-Co(tet*d*)$(OH_2)_2^{3+}$ complex may be assigned the (VfCE)[7] stereochemistry.



(VfCE)

Although one might expect methyl group pairing in this complex due to the similarity of the chelate ring conformations,[7] examination of molecular models shows that the environment of each methyl group is different, in agreement with the observed pmr spectrum. This observation again emphasizes that even in the limited sense of our definition[18] small upfield or downfield chemical shifts are not sufficient to distinguish axial from equitorial methyl groups; the topology of the local induced magnetic field is difficult to know in advance.

The observation that the mixture of *trans*-Co(tet*d*)$(OH_2)_2^{3+}$ complexes returns nearly completely to α-*cis*-Co(tet*d*)$(OH_2)_2^{3+}$ on standing for a week and a half suggests that isomeric equilibrium is more readily achieved, and the *cis*-geometry is relatively more stable among these complexes than among the Co(tet*b*)$(OH_2)_2^{3+}$isomers. This observation also demontrates that α-*cis*-Co(tet*d*)$(OH_2)_2^{3+}$ is the most stable of those complexes easily reached in stepwise isomerization reactions (Figure 9). Actually the tet*d* stereochemistries which Whimp, Bailey, and Curtis[7] considered to be lowest in energy are closely related through stepwise isomerizations, and we have indicated in Figure 9 the logical assignement of the stereochemistry of the few isomers which we have observed. There is no clear basis for assignment of the stereochemistry of the β-*trans*-Co(tet*d*)$(OH_2)_2^{3+}$ complex, although analogy to the tet*b* case makes the allegedly higher energy ligand conformation, (IIIBA), an attractive choice. It is also a possibility that the substance we have designated β-*trans*-Co(tet*d*)$(OH_2)_2^{3+}$ is a mixture of (IIIBA) and (IAA).

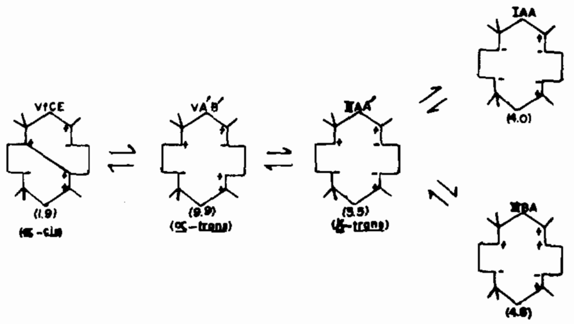
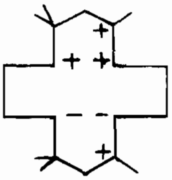
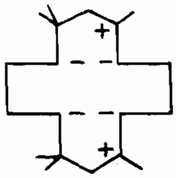


Figure 8. Probable stepwise isomerization reactions of α-*cis*-Co(tet*d*)$(OH_2)_2^{+3}$. Only the most stable isomers, according to ref. 7, are included. See caption to Figure 7 for notation.



(IIIBA)



(IAA)

C. *Some Problems of Stability and Chemical Reactivity of Stereoisomers.*

In their examination of acid hydrolysis rates in $CoLCO_3^+$ complexes, Kernohan and Endicott[4] attributed the exceptionally slow hydrolysis are for Co(tet*d*)CO_3^+ to « stereochemical protection » of the carbonate group relative to replacement by two water molecules. If this argument is correct and if one uses $Co(en)_2CO_3^+$ as an approximate reference for the case of no stereochemical protection, then α-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$ is about 5.5 kcal/mole less stable than α-Co(tet*b*)CO_3^+. From our studies of isomerization reactions in acidic solution we conclude that α-*cis*-Co(tet*b*)$(OH_2)_2^{3+}$ is not much more stable than some of the closely related (*i.e.*, in the sense of Figure 7) *trans*-isomers (but note that some of the isomerization reactions are very slow and equilibrations difficult to achieve). Whimp, *et.al.*[7] predicted that the α-*cis* isomer should be more stable by about 3 kcal/mole than any of the trans isomers of Ni(tet*b*)$_2^+$; in the Co(tet*b*)-$(OH_2)_2^{3+}$ complexes the difference in stability must be less thant one third of that value.

A very interesting observation is that while the α-*cis*-Co(tet*b* and tetd)$(OH_2)_2^{3+}$ complexes are the most stable isomers, *cis* complexes with anionic ligands rapidly isomerize to *trans* geometries. The most striking example of this is the transformation of these α-*cis*-CoL$(OH_2)_2^{3+}$ complexes rapidly and cleanly into the α-*trans*-CoLCl$_2^+$ complexes in acid solution. Due to the increased nonbonded steric repulsions between groups and chelate ring strain in the macrocyclic ligand, the α-*trans* ligand conformations have been estimated to be 6 and 8 kcal/mole less stable than their *cis* counterparts, respectively for tet*b* and tet*d*. If H_2O and Cl^- are assumed to be about the same size (recall also that OH^- similarly « destabilizes » the *cis* complexes), then substitution of the anion for water may result in a repulsive (or solvation) interaction of the order of 10 kcal/mole between the anionic ligands.

The tet*b* and tet*d* complexes of cobalt(III) are relatively labile, as noted above, and relatively fragile. Solutions of the diaquo complexes are not stable in weakly acidic solutions for long periods at room temperature or short periods at 75° - 100°. The decomposition reactions are very complex, but appear to involve the highly energetic dissociation of the macrocyclic ligand to form, eventually Co^{2+}, free ligand, and some oxidized ligand fragments. It is mechanistically significant that this decomposition reaction is repressed in very strong acid, so must involve conformational changes around coordinated amines; that it involves the intermediacy of the *cis*-CoL$(OH_2)_2^{3+}$ complexes and has a very high activation barrier. These observations suggest a mechanism involving the stepwise dissociation of the macrocyclic ligand.