was cooled with running water or ice and filtered. The crude nitrate was then dissolved in a minimum quantity (a little more than 1 l.) of 0.5% nitric acid and the solution was filtered. The pure nitrate can then be precipitated out by adding concentrated nitric acid of about one-fifth the volume of the solution and then cooling to 5°. Light-colored fluffy precipitate may first form, which will be changed to dark green prisms on standing. The precipitate was filtered and washed with dilute nitric acid and ethanol; yield *ca.* 9 g from 10 g of crude sulfate or 14–15 g (28–30%) from 50 g of cobalt(II) nitrate hexahydrate.

Anal. Calcd for $[(NH_3)_4Co\text{-}\mu\text{-}NH_2\text{-}\mu\text{-}O_2\text{-}Co(NH_3)_4](NO_3)_4$: Co, 21.42; N (ammoniacal), 22.91. Found: Co, 21.49; N (ammoniacal), 22.76.

10. μ-Amido-μ-peroxo-bis(tetraamminecobalt)(4+) Tetrachloride Dihydrate. To a suspension of 5 g of crude μ-amido-μ-peroxo-bis(tetraamminecobalt)(4+) sulfate dihydrate in 30 ml of water was added 20 ml of concentrated hydrochloric acid with stirring, 30 ml of ethanol was added to it, and the mixture was cooled with ice. The crude chloride thus formed was filtered by suction and dissolved in 50 ml of 0.1 *M* hydrochloric acid. After filtration 30 ml of concentrated hydrochloric acid (12 *M*) and 50 ml of ethanol were added and the mixture was cooled with ice. The precipitate was filtered and washed with ethanol; yield 3.5 g.

Anal. Calcd for $[(NH_3)_4Co\text{-}\mu\text{-}NH_2\text{-}\mu\text{-}O_2\text{-}Co(NH_3)_4]Cl_4 \cdot 2H_2O$: Co, 24.56; N, 26.26; Cl, 29.55. Found: Co, 24.42; N, 26.04; Cl, 29.73.

Semiquantitative Study of the Change of the Monobridged Complex to the Dibridged One. There were many factors which made this kind of experiment a difficult and incomplete one, but the results obtained at least give a general idea of the formation of the dibridged complex from the monobridged one and approximately the best conditions for preparation of the dibridged complex. For example, since the starting monobridged complex decomposes violently when brought in contact with aqueous ammonia at the reaction temperature from the outset, the complex (4 g of the anhydrous nitrate) was actually dissolved in cold aqueous ammonia (100 ml) and brought to the reaction temperature in the course of 5 min.

Oxidation of the dibridged complex formed was done by pouring an aliquot (2 ml) of the reaction mixture into a shaken 10% solution (5 ml) of $(NH_4)_2Ce(NO_3)_6$ in 6 *N* HNO_3 which had been chilled in a Dry Ice–acetone bath. The mixture was kept in a refrigerator for 1–2 days. The paramagnetic dibridged complex was extracted from the precipitate with ~1–3-ml portions of 0.3 *N* HNO_3, precipitated as the sulfate, and dissolved in 3 *N* perchloric acid. The amount of the complex was then estimated by the absorbance measurement at 700 mμ (ε 310).

The unreacted monobridged peroxo complex was oxidized by pouring a different aliquot (2 ml) into a mixture of 0.5 g of ammonium nitrate and 0.3 g of ammonium persulfate. After ~30–60 min, the mixture was acidified with dilute nitric acid and allowed to stand. The paramagnetic monobridged complex was extracted from the precipitate with 3 *N* perchloric acid and evaluated by use of absorbance measurements at 670 mμ (ε 822). The efficiency of the recovery of the dibridged and the monobridged complexes in the above procedures has been found to be ~96 and ~82%, respectively, but no correction factors for this efficiency were applied for the data in Figure 1.

Acknowledgments. We thank Mrs. Judith K. Kinnaird for her able assistance with some of the experimental work. We are grateful also to the ANL Analytical group, particularly to Mr. Adolph Venters and Mr. Lloyd F. Krout, for their help with the analytical work. We also express our hearty gratitude to Professor Nobukazu Okazaki and Dr. Akiko Okumura of the Nara Women's University for their kind offer of laboratory facilities, cooperation in the isotopic experiments, and helpful discussions regarding the reduction reaction of the paramagnetic dibridged complex in aqueous ammonia.

Hindered Ligand Systems. *cis,cis*-Triaminocyclohexane and Its Complexes with Trivalent Cobalt and Rhodium

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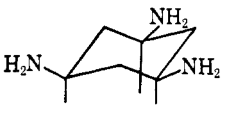
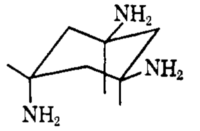
Received July 24, 1967

Abstract: The Birch reduction of the trioxime of α-phloroglucinol is shown to produce both *cis,cis*-1,3,5-triaminocyclohexane (*cis,cis*-tach) and the *cis,trans* isomer in nearly equal proportions. However, under the prevailing conditions, only the former reacts with Co(III) or Rh(III) to form stable bis complexes, whose ligand field spectra indicate that they must consist of nearly regular octahedra. Furthermore, the ligand field parameters are nearly identical with those of $Co(en)_3^{3+}$ and $Rh(en)_3^{3+}$. However, a noticeable difference occurs in the charge-transfer spectrum of $Co(\mathit{cis,cis}\text{-tach})_2^{3+}$, when compared to that of $Co(en)_3^{3+}$. A qualitatively simple explanation involving orbital misdirection is tentatively offered. In addition, the decomposition of $Co(\mathit{cis,cis}\text{-tach})_2^{3+}$ has led to the isolation of the free ligand, whose proton magnetic resonance spectrum compares favorably with known compounds of similar stereochemistry. It is also suggested that the sodium-in-alcohol reduction of the trioxime produces both isomers of the triamine.

The synthesis of 1,3,5-triaminocyclohexane (tach) was first accomplished in poor yields by Hassel and Lunde[1] through the reduction of the corresponding oxime with sodium in alcohol. Although two geometric isomers are possible (see structures below), it would appear that the X-ray data[1,2] indicated that the product consisted exclusively of the isomer with all amine groups disposed in equatorial positions, or *cis,cis*-tach. Internal rotation of this interesting ligand causes the amine groups to move into a triaxial conformation wherein, if normal bond lengths and angles are maintained, the nitrogen atoms should describe an



cis,cis



cis,trans

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[1] O. Hassel and K. Lunde, *Research* (London), 3, 484 (1950).

[2] P. Andersen and O. Hassel, *Acta Chem. Scand.*, 5, 1349 (1951).

equilateral triangle whose edge is about 2.5 Å. This distance compares favorably with the edges of the trigonal faces of the octahedra formed by many metal ions in their complexes with ammonia and amines. While this consideration points to the potentialities of the ligand, studies of its reactions were undoubtedly thwarted by the relatively poor preparative procedure that was available.

Lions and Martin[3] subsequently reported an improved preparation of the amine by the Birch reduction and studied the reactions of a number of Schiff bases derived from the amine. The sexadentate condensates with salicylaldehyde and pyridine-2-aldehyde were shown to form complexes with Fe(II), Co(II), and Co(III) in yields which, when quoted, were universally low. Brauner and Schwarzenbach,[4] apparently assuming that this preparative procedure was stereospecific, completed potentiometric studies of the stabilities of complexes of the amine with a number of metal ions. The results indicated the facile deprotonation of M(*cis,cis*-tachH)$^{3+}$ to yield M(*cis,cis*-tach)$^{2+}$ (M = Cu and Zn). It was thought that in the former the ligand was bidentate and in the boat form, but in the latter the loss of a proton enabled the ligand to achieve the tridentate and triaxial chair conformation. Similar complexes were formed with Ag(I), but complex formation with Ni(II), Co(II), and Cd(II) was found to be negligible. The formation of bis complexes was not studied. Subsequently, Bosnich and Dwyer,[5] again using the same preparative method for the amine, reported the preparation of Co(*cis,cis*-tach)(NO$_2$)$_3$ in an exceptionally high yield.

There would appear to be no completely convincing argument against the formation of stable bis complexes, at least with certain metal ions. Molecular models of M(*cis,cis*-tach)$_2$$^{n+}$, using metal–nitrogen bond distances typical of compounds containing metal ions of the first transition series, reveal no serious nonbonded interactions between the amine protons of the adjacent ligands. In addition, the stepwise formation constant for M(*cis,cis*-tach)$_2$$^{n+}$ should compare favorably[6] to that of M(*cis,cis*-tach)$^{n+}$, except perhaps for those cases involving metal ions which possess Jahn–Teller instability. In order to explore the possibility of the formation of M(*cis,cis*-tach)$_2$$^{n+}$ complexes, the reactions of the ligand with various transition metal ions have been examined. The research described in this paper led to the isolation of the Co(*cis,cis*-tach)$_2$$^{3+}$ and Rh(*cis,cis*-tach)$_2$$^{3+}$ cations. Of equal importance was the discovery that the Birch reduction, and probably the sodium-in-alcohol reduction, can produce both stereoisomers of tach, but that only *cis,cis*-tach is apparently capable of the formation of stable complexes with Co(III) and Rh(III).

Experimental Section

1,3,5-Triaminocyclohexane. This compound was prepared from the trioxime of α-phloroglucinol according to the method of Lions and Martin,[3] but using redistilled ammonia and cooling the reaction mixture in a Dry Ice–acetone bath during the addition of sodium. Acidification of a small quantity of the amine with dilute HCl led to the preparation of an analytical sample of tach·3HCl·H$_2$O. *Anal.* Calcd for $C_6H_{20}N_3Cl_3O$: C, 28.08; H, 7.86; N, 16.38. Found: C, 28.08; H, 7.85; N, 16.30.

Co(*cis,cis*-tach)$_2$(ClO$_4$)Cl$_2$. To 7.95 g of Na$_3$Co(CO$_3$)$_3$·3H$_2$O was added 5.74 g of tach, followed by 2 ml of 4 *M* HClO$_4$ and 30 ml of 4 *M* HCl. This solution was heated on a steam bath until the evolution of CO$_2$ had ceased. Orange crystals deposited as the reaction proceeded. An additional 2 ml of concentrated HClO$_4$ and 10 ml of concentrated HCl were added, and the mixture was cooled in ice. After filtration, the product was washed with 10 ml of 4 *M* HCl. Recrystallization from hot 4 *M* HCl (to which a few drops of concentrated HClO$_4$ had been added) produced typically about 3.0 g (30% yield based on the amine) of orange, hexagonal plates. *Anal.* Calcd for $CoC_{12}H_{30}N_6Cl_3O_4$: C, 29.55; H, 6.20; N, 17.23; Cl, 14.54. Found: C, 29.72; H, 6.20; N, 17.57; Cl, 14.6. Additional confirmation for the presence of perchlorate came from the infrared spectrum which contained a band at 1090 cm^{-1} typical of the strongest absorption of that anion.

This salt is considerably less soluble than either the triperchlorate or the trichloride.

Co(*cis,cis*-tach)$_2$(ClO$_4$)$_3$. This salt was prepared by passing aqueous solutions of Co(*cis,cis*-tach)$_2$(ClO$_4$)Cl$_2$ through an anion-exchange column in the perchlorate form. Evaporation gave orange, hexagonal plates. *Anal.* Calcd for $CoC_{12}H_{30}N_6Cl_3O_{12}$: C, 23.41; H, 4.91; N, 13.65. Found: C, 23.54; H, 4.84; N, 13.55. Conductivity measurements[8] of 3.09 $\times$ 10^{-3} *N* solutions indicated a conductivity of 111.5 mhos cm^2 equiv^{-1} at 25°.

Co(*cis,cis*-tach)$_2$Cl$_3$·0.75HCl·4H$_2$O and Co(*cis,cis*-tach)$_2$Cl$_3$. When aqueous solutions of Co(*cis,cis*-tach)(ClO$_4$)Cl$_2$ were passed through an anion-exchange column in the chloride form, orange, hexagonal plates were obtained after the addition of concentrated HCl and evaporation. When dried in air, these crystals contained both water and hydrogen chloride of crystallization. *Anal.* Calcd for $CoC_{12}H_{38.75}N_6Cl_{3.75}O_4$: C, 27.55; H, 7.47; N, 16.07; Cl, 25.42. Found: C, 27.75; H, 7.56; N, 16.06; Cl, 25.7. When dried at 100° for 8 hr, the solvate-free form was obtained. *Anal.* Calcd for $CoC_{12}H_{30}N_6Cl_3$: C, 33.95; H, 7.07; N, 19.80; Cl, 25.20. Found: C, 34.30; H, 6.93; N, 19.93; Cl, 25.2.

Co(*cis,cis*-tach)$_2$Br$_3$ and Co(*cis,cis*-tach)$_2$I$_3$. These salts were prepared in solution for spectrophotometric purposes by passing solutions of Co(*cis,cis*-tach)$_2$(ClO$_4$)Cl$_2$ through an anion-exchange column in the appropriate form. Addition of the appropriate hydrohalic acid to small portions of these solutions produced orange, hexagonal plates in each case. The composition of these crystals was not investigated, but it is worthy to note that the iodide appears to be more insoluble than Co(*cis,cis*-tach)$_2$(ClO$_4$)Cl$_2$.

Co(*cis,cis*-tach)(NO$_2$)$_3$. When prepared according to the method of Bosnich and Dwyer[5] and dried in air, the complex was obtained in 42% yield (based on the amine) in the form of a hydrate. The results agree well with Co(*cis,cis*-tach)(NO$_2$)$_3$·0.8H$_2$O. *Anal.* Calcd for $CoC_6H_{16.6}N_6O_{6.8}$: C, 20.62; H, 5.03; N, 24.08. Found: C, 20.62; H, 5.06; N, 24.04. Bosnich and Dwyer reported the anhydrous compound in 90% yield.

Rh(*cis,cis*-tach)$_2$(ClO$_4$)$_3$. A concentrated aqueous solution containing 0.50 g of tach and 0.25 g of RhCl$_3$·3H$_2$O was heated at 100° for 8 hr in a nitrogen atmosphere. The solution was then evaporated to a small volume and absolute ethyl alcohol was added. The crude product which precipitated was filtered, washed with alcohol, and dried in air. Purification was accomplished by two recrystallizations from concentrated HCl. The resulting white, hexagonal plates apparently contain both water and hydrogen chloride of crystallization, but a satisfactory analysis for the solvate-free salt could not be obtained even after drying at 120° for 72 hr. However, when solutions of the chloride were passed through an anion-exchange resin in the perchlorate form and evaporated, colorless needles of the perchlorate were obtained. *Anal.* Calcd for Rh-

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(3) F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **79**, 1572 (1957).

(4) P. A. Brauner and G. Schwarzenbach, *Helv. Chim. Acta*, **45**, 2030 (1962).

(5) B. Bosnich and F. P. Dwyer, *J. Australian Chem. Soc.*, **19**, 2045 (1966).

(6) Bonding in each case must be accompanied by the endothermic conversion of the triequatorial conformer into its triaxial counterpart. The energetics of this process would be difficult to estimate with accuracy. If it is assumed that the amine group, with its lone pair, is sterically similar to a methyl group, then the triequatorial conformation of *cis,cis*-tach should be favored by about 11 kcal mole^{-1}, or three times the experimentally observed value of 3.7 kcal mole^{-1} for two diaxial methyl groups.[7] It is conceivable that this process could cause the addition of a second ligand molecule to be unfavorable under certain circumstances.

(7) N. Allinger and M. A. Miller, *J. Am. Chem. Soc.*, **83**, 2145 (1961).

(8) For Co(pn)$_3$(ClO$_4$)$_3$ in 3.34 $\times$ 10^{-3} *N* solutions, Λ = 114.75 mhos cm^2 equiv^{-1}: R. A. Wynveen, J. L. Dye, and C. H. Brubaker, Jr., *J. Am. Chem. Soc.*, **82**, 4441 (1960).

Table I. Comparison of the Electronic Spectra of M(*cis,cis*-tach)$_2^{3+}$ with M(en)$_3^{3+}$ [a,b]

	Co(*cis,cis*-tach)$_2^{3+}$	Co(en)$_3^{3+}$	Rh(*cis,cis*-tach)$_2^{3+}$	Rh(en)$_3^{3+}$
$^1A_1 \rightarrow {}^3T_1$	13,100 (0.4)	13,800	...	...
$^1A_1 \rightarrow {}^1T_1$	20,900 (75)	21,470	33,300 (191)	33,200
$^1A_1 \rightarrow {}^1T_2$	29,200 (75)	29,500	39,500 (182)	39,600
CT	41,700 (17,900) ~46,000 (11,000)	47,200[c]	...	...
$\Delta/10$	2,480	2,530	3,640[d]	3,640[d]
B	520	502	388	400
C	3,900	3,835	3,104[d]	3,200[d]

[a] Band positions are in cm^{-1}. [b] Values in parentheses refer to the molar extinction coefficients. [c] Reference 13. [d] Computed by using the assumption $C = 8B$, as is approximately the case with the cobalt complexes.

$C_{12}H_{30}Cl_3O_{12}$: C, 21.85; H, 4.58; N, 12.74. Found: C, 21.94; H, 4.72; N, 12.84.

Separation of the Isomers of tach. Samples consisting principally of the *cis,trans* isomer were recovered from the filtrate of a reaction of tach with $Na_3Co(CO_3)_3 \cdot 3H_2O$. The filtrate was reduced in volume and boiled with decolorizing charcoal. After filtration and evaporation, the solid product was recrystallized from HCl until no further contamination with cobalt salts was observed. Finally, all remaining perchlorate anion was removed by passage through an anion-exchange column in the chloride form. Crystallization from HCl led to *cis,trans*-tach·3HCl·H_2O in about 77% isomeric purity (estimated from pmr spectrum).

The *cis,cis* isomer was recovered by refluxing Co(*cis,cis*-tach)$_2$-(ClO_4)Cl_2 in 6 *M* NaOH in a nitrogen atmosphere. After 8 hr, the solution was cooled, filtered, and passed through a cation-exchange column in the hydrogen form to remove most of the metallic cations and to neutralize the solution. Crystallization was obtained by addition of concentrated HCl. Recrystallization from HCl until the characteristic color of the Co(II) was removed gave *cis,cis*-tach·3HCl·H_2O.

Anal. Calcd for $C_6H_{20}N_3Cl_3O$: C, 28.08; H, 7.86; N, 16.38. Found for the *cis,trans* isomer: C, 28.24; H, 7.75; N, 16.62; Found for the *cis,cis* isomer: C, 28.34; H, 7.63; N, 16.27.

Instrumentation. All spectroscopic equipment has been previously described.[9] In addition, the conductance measurements were obtained using a Serfass conductivity bridge, Model RCM15. Cr Kα X-radiation was used to obtain powder patters of the complexes, while Cu Kα radiation was used with the free ligand. All pmr spectra are relative to TMS (internal capillary).

Discussion of Results

The Complexes. The reaction of the triamine (isolated from the Birch reduction) with Co(CO_3)$_3^{3-}$ has produced a single complex ion, Co(*cis,cis*-tach)$_2^{3+}$, which was obtained in the form of several salts. The isolation of the anhydrous perchlorate eliminates the possibility that the complex ion includes a coordinated water molecule. Furthermore, the electronic spectrum of this ion (Figure 1 and Table I) is similar to that of Co(en)$_3^{3+}$ and points unambiguously to the presence of six amine groups bonded to a cobalt atom. In Table I, the usual spectroscopic parameters are seen to compare very favorably to those of Co(en)$_3^{3+}$. In addition, the equivalent conductance of the perchlorate salt is nearly identical with that of Co(pn)$_3$(ClO_4)$_3$ in solutions of the same concentration.[8] Thus, the complex ion must be mononuclear in nature and does not consist of a polymeric structure containing the triequatorial conformer of the ligand. Unambiguous proof for the presence of the symmetric stereoisomer in the complex will be presented in the next section.

It was also found the Rh(*cis,cis*-tach)$_2^{3+}$ has an electronic spectrum which closely matches that of Rh(en)$_3^{3+}$. In addition, the infrared spectra of the cobalt and rhodium complexes (Table II) are nearly identical, both in band position and band intensity. However, X-ray powder photographs of the two perchlorate salts are not similar, as shown in Table II. Since compounds of trivalent cobalt are generally isomorphous with their rhodium analogs, it might be concluded that these complexes are not isostructural. However, the close correspondence of their infrared spectra would not support this argument. The minor differences in their spectra are probably attributable to lattice effects, which in turn may be related to size differences of the metal atoms (see below).

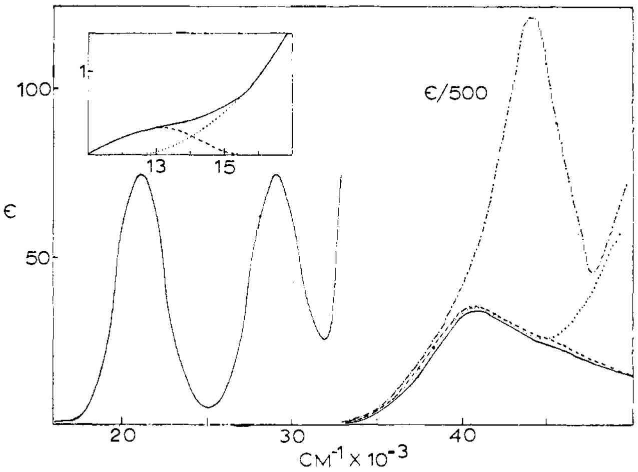

Figure 1. The electronic spectrum of Co(*cis,cis*-tach)$_2^{3+}$ in the presence of various anions: (——) ClO_4^-, (- - - -) Cl^-, (· · · ·) Br^-, and (–·–·–·) I^-.

The pmr spectra of these ions also provide results which, while consistent with a structure containing the triaxial conformation of the ligand, do not entirely eliminate other possibilities. With the cobalt complex, facile exchange of the amine protons with deuterons occurs upon solution in D_2O. The spectrum, neglecting that portion arising from this exchange, only consists of two featureless peaks at δ 2.08 and 3.07 with an intensity ratio of 2:1. These absorptions must then be due to the methylene and methine hydrogens, respectively. The widths of each peak at half-height are 6 and 10 cps. Since the methylene hydrogens cannot be equivalent even in a nonrigid structure, their chemical shifts must only differ by less than about 6 cps. Furthermore, the width of the resonance at δ 3.07 is such that it is impossible to conclusively prove the equivalence of the methine hydrogens. The similarity of this spectrum to that of the rhodium complex, which has absorptions at δ 2.51 and 3.80 with similar line widths, suggests again that the two complexes are structurally similar. Furthermore, neither spectrum rules out a pseudo-ada-

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(9) R. Saillant, J. L. Hayden, and R. A. D. Wentworth, *Inorg. Chem.*, 6, 1497 (1967).

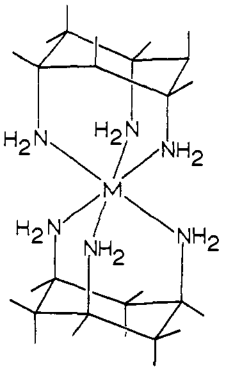

Figure 2. The proposed structure for M(*cis,cis*-tach)$_2$$^{3+}$ (M = Co and Rh).

mantane structure. Both spectra, however, contrast markedly with those of 2,8,9-trioxaphosphaadamantane[10] and its complexes,[11,12] wherein the resonance due to the axial hydrogens is well resolved from that due to the equatorial hydrogens. Geminal coupling is also readily discerned in those spectra.

Table II. Infrared and X-Ray Spectra of M(*cis,cis*-tach)$_2$(ClO$_4$)$_3$

	M = Co	M = Rh
Infrared[a]	3200 (s), 3100 (s), 1600 (m), 1560 (s), 1450 (m), 1430 (w), 1380 (m), 1280 (w), 1220 (m), 1160 (sh), 1130 (s), 1080 (s), 1050 (sh), 965 (w), 917 (m), 758 (w)	3190 (s), 3100 (sh), 1620 (m), 1570 (s), 1460 (m), 1440 (w), 1380 (m), 1280 (m), 1220 (s), 1150 (w), 1120 (s), 1080 (s), 1050 (s), 960 (w), 917 (m), 760 (w)
X-Ray[b]	10.7 (s), 7.22 (w), 6.55 (m), 6.07 (s), 5.31 (w), 5.21 (w), 4.57 (w), 4.15 (w), 3.77 (s), 3.55 (m), 3.08 (s), 2.65 (m), 2.58 (m), 2.47 (w), 2.17 (m), 2.13 (w), 2.01 (w), 1.86 (m), 1.78 (m), 1.69 (w), 1.61 (w), 1.43 (m), 1.41 (w), 1.38 (w)	9.24 (m), 8.62 (s), 7.13 (w), 6.82 (w), 4.89 (w), 4.78 (w), 4.43 (s), 4.23 (m), 4.17 (m), 3.43 (w), 3.34 (w), 3.30 (w), 3.20 (w), 3.19 (w), 2.93 (w), 2.67 (w), 2.62 (w)

[a] All values in wave numbers: s = strong, m = medium, w = weak, and sh = shoulder. [b] Expressed as *d* spacings.

The proposed structure for the complex ion is shown in Figure 2. It is evident from this figure that the size of the metal ion may play an important role in determining the extent of distortions, both within the MN$_6$ octahedron and within the ligand moiety. For example, if all bond distances and angles within the triaxial conformation of the ligand are normal, then the nitrogen atoms will describe a triangle whose edge is 2.5 Å. With a strictly regular octahedron, the nitrogen–metal bond distances would then be about 1.8 Å. While this distance is somewat smaller than the typical bond distances of 1.9–2.0 Å found in many amine complexes of trivalent cobalt, it is considerably less than the distances expected to occur in similar complexes of metals of the second transition series. More reasonable bond distances can be obtained by either enlarging the triangle of nitrogen atoms or by increasing the distance between the plane containing the nitrogen atoms and the metal ion. Both of these possibilities will introduce distortions into the MN$_6$ octahedron, but only the former will simultaneously introduce distortions into the ligand framework. Opposing any major tendency toward distortion, however, will be immense ligand field stabilization energy associated with the d^6 electronic configuration in a regular octahedral field. Thus, as a consequence of the size of the metal ion as well as its ligand field stabilization energy, several factors will play important roles in fixing the structure of the complex ion. While the ligand field spectra indicate that the nitrogen–metal bond distances are probably normal, it is not unlikely that small distortions introduced through these effects may be of sufficient magnitude to explain the lack of isomorphic character and the minor differences in the infrared spectra. The consequences of these distortions would not generally be observed in the ligand field spectra when the measurements are performed with solutions. However, the charge-transfer spectra may be a sensitive gauge for distortions of this nature.

Since the ligand field spectrum of Co(*cis,cis*-tach)$_2$$^{3+}$ is similar to that of Co(en)$_3$$^{3+}$, it may be concluded that the energy of the $t_{2g} \rightarrow e_g^*$ transition in these ions is also similar, as evidenced by their nearly identical values of Δ. However, their charge-transfer spectra differ considerably. While the first charge-transfer absorption[13] in Co(en)$_3$$^{3+}$ occurs at 47,200 cm^{-1}, intense absorptions at 41,700 and 46,000 cm^{-1} occur with Co(*cis,cis*-tach)$_2$$^{3+}$. Experiments with various anions (Figure 1) have indicated that the absorptions in the presence of ClO$_4^-$ or Cl$^-$ ions are not due to those induced by a polarizable anion. The anion–complex charge-transfer spectrum is only partially visible in the presence of Br$^-$ ion and completely visible with I$^-$ ion. In the absence of this effect, the observed spectrum must be due to transitions from the filled bonding orbitals to the vacant e_g^* orbitals. The absorption at 41,700 cm^{-1} is assuredly due to the $t_{1u} \rightarrow e_g^*$ transition. However, the origin of the absorption at 46,000 cm^{-1} is obscure. It is either a component of the $t_{1u} \rightarrow e_g^*$ transition arising from interelectronic repulsion ($t_{1u} \times e_g = t_{1u} + t_{2u}$), or a component arising from a trigonal distortion. Alternatively, the $a_{1g} \rightarrow e_g^*$ transition is a possibility, although it is forbidden by the electric dipole selection rules. Furthermore, it would presumably lie at far greater energies. Thus, one of the first two possibilities seems more probable. Nevertheless, the decrease in wave numbers of the absorptions in Co(*cis,cis*-tach)$_2$$^{3+}$, when compared to Co(en)$_3$$^{3+}$, implies that the energy separating the bonding orbitals and the e_g^* orbitals has decreased.

A qualitatively simple, although not necessarily accurate, explanation for this phenomenon would involve orbital misdirection. If it is assumed that within this complex a nearly regular octahedron is obtained and that sp^3 hybridization is maintained on the nitrogen atoms, then the lone pairs will not be directed toward the cobalt atom, and the extent of misdirection would be ideally about 16°. Since both σ and π contributions from a lone pair are then possible, a trigonal electronic

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(10) J. G. Verkade and R. W. King, *Inorg. Chem.*, **1**, 948 (1962).

(11) J. G. Verkade, R. W. King, and C. W. Heitsch, *ibid.*, **3**, 884 (1964).

(12) D. G. Hendricker, R. E. McCarley, R. W. King, and J. G. Verkade, *ibid.*, **5**, 639 (1966).

(13) A. V. Kiss and D. V. Czegledy, *Z. Anorg. Allgem. Chem.*, **235**, 407 (1938).

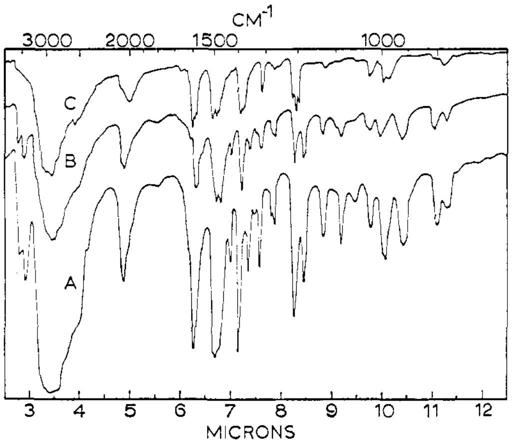


Figure 3. Infrared spectra: (A) mixed isomers of tach·3HCl·H_2O obtained from the Birch reduction; (B) product consisting principally of *cis,trans*-tach·3HCl·H_2O; (C) *cis,cis*-tach·3HCl·H_2O.

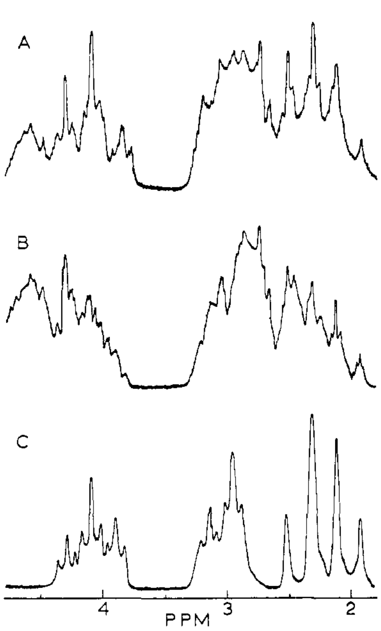
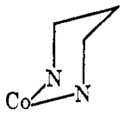


Figure 4. Proton magnetic resonance spectra: (A) mixed isomers of tach·3HCl·H_2O obtained from the Birch reduction; (B) product consisting principally of *cis,trans*-tach·3HCl·H_2O; (C) *cis,cis*-tach·3HCl·H_2O.

distortion of symmetry D_{3d} will result. Furthermore, since the metal p orbitals are more intimately involved in bonding than the d orbitals, it could reasonably be expected that the largest effect of this distortion would occur in the charge-transfer spectrum and not in the ligand field spectrum. Thus, the $t_{1u} \rightarrow e_g^*$ transition would be affected to a larger extent than the $t_{2g} \rightarrow e_g^*$ transition.[14,15] It is of interest to note that a regular decrease in wave numbers for the first charge-transfer absorption occurs[16] such that $Co(NH_3)_6^{3+}$ > $Co(en)_3^{3+}$ > $Co(tn)_3^{3+}$ $\sim$ Co(*cis,cis*-tach)$_2^{3+}$ (using the mean of the two absorption maxima). This trend may be associated to some extent with the effects which have been discussed. Trigonal distortions of the metal orbitals may also be important, but the relative importance of the two effects would be difficult to assess, since equilibrium values for these angles within the complex ion in solution are not available.[17] However, in $Co(tn)_3^{3+}$ the preferred confirmation of the metal–ligand ring should be identical with the six nitrogen-containing ring systems in Co(*cis,cis*-tach)$_2^{3+}$. Thus similar distortions may result and it may not be surprising that their charge-transfer absorptions, though not identical, occur at similar wave numbers.



The Ligand and Its Isomers. The decomposition of Co(*cis,cis*-tach)$_2^{3+}$ and Co(*cis,cis*-tach)$(NO_2)_3$ led to the isolation of *cis,cis*-tach·3HCl·H_2O. In Figures 3 and 4, the infrared and pmr spectra of this compound are compared with those of the trihydrochloride monohydrate of the amine obtained from the Birch reduction. It is evident that the recovered ligand has a far simpler spectrum in each case than the original material.

In the pmr spectrum of the symmetric isomer, the quartet centered at δ 2.23 has been assigned to the axial methylene hydrogen, while the doublet centered at δ 3.13 is its equatorial counterpart. Finally, the triplet at δ 4.11 is due to the methine hydrogen. Superimposed on each of the last two sets of resonances is a set of triplets separated by 3 cps. These features, whose assignments are in accord with the integrated intensities, remain unchanged upon the addition of NaOD. Simple first-order analysis of the spectrum leads to the coupling constants shown in Table III. It is noteworthy that the spectrum of this compound is identical in appearance with the high-field portion of the spectrum[21] of *cis,cis*-1,3,5-tris(4-pyridyl)cyclohexane. Coupling constants for this compound, as well as those recently derived[22] for *cis,cis*-1,3,5-trimethylcyclohexane, are shown in Table III and compare favorably with those of this isomer of tach.

From the solutions used in the preparations of Co(*cis,cis*-tach)$_2^{3+}$, it was also possible to isolate another substance whose properties[23] correspond to those ex-

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(14) Arguments pertaining to the effect of orbital misdirection on the optical activity of transition metal complexes of trigonal symmetry have been given by A. D. Liehr, *J. Phys. Chem.*, **68**, 665 (1964).

(15) An explanation involving orbital misdirection, which is not based on an accurate knowledge of the atomic positions, is necessarily tenuous. Even if atomic positions were known (which would be doubtful in the case of the amine protons), bond misdirection appears to be virtually impossible to prove or disprove. In this regard, see the excellent review by W. H. Flygare, *Science*, **140**, 1179 (1963). Nevertheless, it offers an attractively simple explanation of the observed phenomena. Other more complex explanations are, of course, possible.

(16) This absorption occurs at about 53,000 cm^{-1} in $Co(NH_3)_6^{3+}$ [12] and at 43,500 cm^{-1} in $Co(tn)_3^{3+}$.

(17) It cannot be assumed that the values for the pertinent angles can be taken from single crystal data. With $Co(en)_3^{3+}$, for example, both the Co–N–C bond angle and the N–Co–N angle are markedly sensitive to the nature of the crystal. The observed[18] Co–N–C angle in Δ-Co-$(en)_3Cl_3 \cdot NaCl \cdot 6H_2O$ is close to the tetrahedral value (observed 109.5°), while the N–Co–N angle is 87.4°. In Δ-$Co(en)_3Br_3 \cdot H_2O$[19] the N–Co–N angles range from 86 to 94°, and in racemic $Co(en)_3Cl_3 \cdot 3H_2O$[20] the Co–N–C angle was found to be 105.4°. It would be unwise to assume that any of these represent the true equilibrium bond angles in the complex when it is in solution. Most probably, the true values lie somewhere between these extremes.

(18) K. Nakatsu, M. Shiro, Y. Saito, and H. Kuroyo, *Bull. Chem. Soc. Japan*, 30, 158 (1957).

(19) K. Nakatsu, *ibid.*, **35**, 837 (1962).

(20) K. Nakatsu, Y. Saito, and H. Kuroyo, *ibid.*, **29**, 432 (1956).

(21) A. Segre, *Tetrahedron Letters*, **17**, 1001 (1964).

(22) A. Segre and J. I. Musher, *J. Am. Chem. Soc.*, **89**, 706 (1967).

(23) In addition to the properties which are described in the text, the apparent proton dissociation constants (uncorrected for the presence of the *cis,cis* isomer) for this isomer have been determined. These are nearly identical with those of the starting material, as well as those of the *cis,cis* isomer. All are in fair agreement with those of Brauner and Schwarzenbach.[4]

Table III. Coupling Constants for *cis,cis*-tach·3HCl·H_2O and Related Compounds[a]

Compound	J_{gem}	J_{aa}	J_{ae}
cis,cis-tach·3HCl·H_2O	12	12	4
cis,cis-1,3,5-Tris(4-pyridyl)cyclohexane	12.5	12.5	2
cis,cis-1,3,5-Trimethylcyclohexane	13	11	3

[a] Constants are in cps.

pected for *cis,trans*-tach·3HCl·H_2O . Its infrared and pmr spectra are shown in Figures 3 and 4. Closer scrutiny reveals that the superimposition of these spectra on those of the *cis,cis* isomer closely duplicates the spectra of the starting material. The infrared spectra also provide further confirmation for the isomeric assignments, since it is a well-known rule that the more symmetric isomer will possess the simpler spectrum. Accordingly, the infrared spectrum of the compound assigned as the *cis,cis* isomer is far less complex than that of the compound which is believed to be principally the *cis,trans* isomer.

The spectroscopic results also provide a means to determine the relative proportions of the two isomers in the starting material. Between δ 3.08 and 3.33 in the pmr spectra there exists a fraction of the signal due to the methylene hydrogens; about 0.18 in the case of the *cis,cis* isomer and about 0.042 for the material which is primarily the *cis,trans* isomer. Assuming that all of the signal in this region is due to the more symmetric isomer, an upper limit to the fraction of this isomer in a mixture can be estimated. Graphical integration indicated that the probable maximum amount of this isomer in the starting material was 48–50%. In addition, the impure *cis,trans* isomer whose spectrum is shown in Figure 4 contained about 23% of the symmetric stereoisomer. The consistency of these estimates is readily verified from the fact that Co(*cis,cis*-tach)(ClO_4)Cl_2 was isolated in 30% yield from this reaction. The unreacted amine must then have contained about 26% of the *cis,cis* isomer, in good agreement with the result obtained from graphical integration. It should be added that the signal at about δ 4.6, although promising for these purposes, was not used due to the nearby water peak whose position was by no means constant.

There is yet another bit of data which supports the result that, at least under the experimental conditions prevailing within this laboratory, the Birch reduction can produce both isomers of tach in about equal proportions.[24] Since the yield of the hydrate of Co(*cis,cis*-tach)(NO_2)$_3$ was 42% based on the amine, this value must represent a minimum quantity of the *cis,cis* isomer within the starting material. However, it must be noted that Bosnich and Dwyer report a 90% yield of the anhydrous form of this compound. It would appear that as yet undetermined experimental conditions may well influence the stereospecificity of the Birch reduction.

Powder diffraction data of the trihydrochloride monohydrate from the starting material are given in Table IV. Surprisingly, these results can be closely reproduced using the unit-cell parameters given by Hassel and Lunde[1] for the hydrochloride of the product obtained from the sodium-in-alcohol reduction. These results are in complete discord with those obtained from *cis,cis*-tach·3HCl·H_2O produced from the decomposition of Co(*cis,cis*-tach)$_2^{3+}$, as shown in Table V. Therefore, the sodium-in-alcohol reduction, which was thought to yield only the more symmetric isomer, apparently also gives about equal proportions of both isomers. There remains, however, the fact that the structural analysis of Andersen and Hassel[2] indicated that the isomer was the more symmetric one. In that work, single crystals were obtained by evaporation of an ethereal solution of the free amine. It may be that the high symmetry of the *cis,cis* isomer leads to a crystalline product which is readily isolable, while the less symmetric isomer crystallizes only with difficulty or not at all. The same explanation would also account for Hassel and Lunde's observation that the powder pattern of the crystalline amine resembled that of *cis,cis*-1,3,5-cyclohexanetriol. It is also interesting to compare the X-ray diffraction data of the symmetric isomer with those of the starting material. Since the powder patterns do not contain any common lines, both isomers are apparently found in the same crystal.

Table IV. Crystallographic Results for tach·3HCl·H_2O Isolated *via* the Birch Reduction

d_{obsd},[a] A	d_{calcd},[b] Å	*hkl*	Intensity
5.47	5.44	201	m
4.75	4.78	211	w
4.30	4.30	022	m
4.15	4.11	311	m
4.00	3.99	121	w
3.66	3.69	221	vs
3.59	3.58	002	w
3.49	3.50	102	vs
3.27	3.28	120	s
3.21	3.21	420	m
3.12	3.10	330	w
3.00	3.01	302	s
2.87	2.87	122	vs
2.58	2.58	322	s
2.49	2.51	040	s
2.44	2.44	032	s

[a] In addition to these lines, eight others at $d > 2.440$ Å were found. These have weak intensities but can be indexed with accuracies similar to those shown above. [b] Calculated for an orthorhombic unit cell using $a_0 = 16.72$, $b_0 = 10.03$, and $c_0 = 7.16$ Å. See ref 1.

Table V. Crystallographic Results for *cis,cis*-tach·3HCl·H_2O

8.83 (w), 5.80 (w), 5.50 (m), 5.05 (s),
4.43 (s), 4.36 (s), 4.24 (m), 4.22 (w),
3.93 (s), 3.81 (m), 3.76 (m), 3.58 (m),
3.49 (m), 3.41 (s), 3.30 (s), 3.23 (s),
3.13 (m), 2.90 (s), 2.84 (m), 2.75 (m),
2.54 (s), 2.64 (*m*), 2.32 (m), 2.27 (s),
2.23 (w), 2.07 (w), 2.04 (w), 1.95 (w)

It is thus abundantly clear that both geometric isomers of tach can result from the Birch reduction. Since their relative proportions may well be determined by the experimental conditions, evidence for their simultaneous presence or absence is required. For this reason, the stability constants determined by Brauner and Schwarzenbach[4] deserve reinvestigation. Contrary to their results which indicated that the formation of complexes with Ni(II) was negligible, the Ni(*cis,cis*-tach)$_n^{2+}$ (n = 1 or 2) ions have been recently isolated. Their properties, as well as those of similar complexes containing other divalent metal ions, will be described in a subsequent publication.

Acknowledgment. This research was supported in part by the National Science Foundation under Grant No. GP-5764.

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[24] The statistical yield would be 3:1 in favor of the *cis,trans* isomer.