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# Metal Ion Promoted Reactions in Organic Synthesis. Intramolecular Condensations between Ligands Containing Amine and Carbonyl Groups

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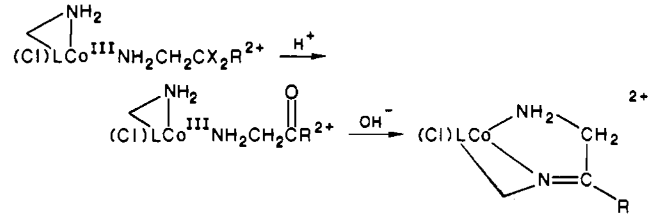
The intramolecular condensation of monodentate (aminomethyl)carbonyl ligands $NH_2CH_2C(=O)R$ (R = H, $CH_3$, phenyl) with quadridentate amines such as tren (tris(2-aminoethyl)amine) and trien (1,8-diamino-3,6-diazaoctane) bound to cobalt(III) ions is explored in terms of controlling the regiospecificity and stereospecificity of such condensations. Chloride ion bound to the pentaaminecobalt(III) directs the condensation to the amine site trans to it via base-catalyzed removal of a proton on the amine. These sites are the most acidic centers in the molecules, and the efficiency of capture of the amido ion by the electrophilic carbonyl center is approximately one in ten proton exchanges. The resultant carbinolamine complexes react further under the basic conditions to imines that can be isolated and then reduced by $BH_4^-$ ion to the fully saturated amine complexes without significant reduction of the Co(III) center. In this manner, chloro–tetraen–cobalt(III) (tetraen = 3,6,9-triazaundecane-1,11-diamine) and chloro–trenen–cobalt(III) isomers (trenen = 3-(2-aminoethyl)-3,6-diazaoctane-1,8-diamine) have been produced regiospecifically. Substituted derivatives of these ligands and attendant complexes have also been synthesized and characterized by X-ray crystallographic methods where necessary and by various spectroscopic techniques. The stabilities of two of the stereoisomers of a *C*-methyl trenen complex have been assessed by molecular mechanics calculations. The kinetics of cyclization of the carbonyl residues were followed in some instances along with proton exchange at the amine sites. Limited aquation and base hydrolysis rate measurements were also made for the chloro–trenen–cobalt(III) ions where the ligand is substituted at C(7) by methyl, phenyl, or imine.

## Introduction

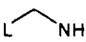
The rational synthesis of multidentate ligands frequently represents a problem of considerable difficulty because of the need to react selectively at one of several similar sites, to avoid polymerization, and to minimize stereochemical complexity.[1-3] A procedure that can eliminate at least some of these difficulties is to conduct the syntheses as a "template reaction" within the coordination sphere of a metal ion.[4] This is not to say that the factors operative in all template reactions are well understood, and indeed, in the case of labile metal ion templates, some confusion over whether thermodynamic or kinetic factors govern the processes exists. Template reactions at inert metal ion centers, therefore, are potentially subject to more subtle applications, provided that the fundamental metal ion chemistry is well enough developed that appropriate reactant species are readily assembled. The detailed synthetic, structural, and kinetic studies that have been made of complexes of cobalt(III) make this an obvious choice of an inert metal ion to employ in the examination of the application of inert metal ion controlled reactions in organic synthesis. Nonetheless, the work that has been done is of quite limited extent,[5-15] and the present work is a contribution to the development of this area.

The condensation of an amine with a carbonyl compound to give, via a carbinolamine, an imine or "Schiff base" is a very well-known reaction.[16] It is of great importance in coordination chemistry not only because imines themselves are excellent ligands but also because so, too, are amines, which are readily produced from imines by reduction.[4,5,6,8,17] However, reactions between free amines and carbonyl compounds do not always give the species desired as ligands, and the use of coordinated metal ions to redirect such reactions is well established.[4] The particular utility for inert metal ions here can be that, under acidic conditions, the metal functions as a protecting group for the amine, allowing elaboration of a carbonyl functionality which can then be condensed with the amine group by rendering the solution basic, so as to partly deprotonate the coordinated amine and thereby allow it to act as a nucleophile. The reactions reported herein are all of this type, being represented by the following general equation:

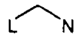


X = OH, $OCH_3$, $OC_2H_5$

$X_2$ = $OCH_2CH_2O$

 = quadridentate amine

Although



could, in principle, be any quadridentate amine incorporating at

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(1) Lions, F. *Rev. Pure Appl. Chem.* **1969**, *19*, 177.
(2) Lehn, J.-M. *Struct. Bonding (Berlin)* **1973**, *16*, 1; *Acc. Chem. Res.* **1978**, *11*, 49. Sargeson, A. M. *Chem. Br.* **1979**, *15*, 23.
(3) Izatt, R. M., Christensen, J. J., Eds. *Synthetic Multidentate Macrocyclic Compounds*; Academic: New York, 1978.
(4) Curtis, N. F. *Coord. Chem. Rev.* **1968**, *3*, 3. Healy, M. De S.; Rest, A. J. *Adv. Inorg. Chem. Radiochem.* **1978**, *21*, 1 and references therein.
(5) References most apposite to the present work are as follows: (a) Bell, J. D.; Gainsford, A. R.; Golding, B. T.; Herlt, A. J.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1974**, 980. (b) Gainsford, A. R.; Sargeson, A. M. *Aust. J. Chem.* **1978**, *31*, 1679. (c) Gainsford, A. R.; Pizer, R. D.; Sargeson, A. M.; Whimp, P. O. *J. Am. Chem. Soc.* **1981**, *103*, 792. An eclectic selection of other works from our laboratories concerning this topic generally is given in ref 6–14.
(6) Golding, B. T.; Harrowfield, J. MacB.; Sargeson, A. M. *J. Am. Chem. Soc.* **1974**, *96*, 3003.
(7) Golding, B. T.; Harrowfield, J. MacB.; Robertson, G. B.; Sargeson, A. M.; Whimp, P. O. *J. Am. Chem. Soc.* **1974**, 96, 3691.
(8) Harrowfield, J. MacB.; Sargeson, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 1514.
(9) (a) Butler, D. G.; Creaser, I. I.; Dyke, S. F.; Sargeson, A. M. *Acta Chem. Scand.* **1978**, *A22*, 789. (b) Creaser, I. I.; Harrowfield, J. MacB.; Keene, F. R.; Sargeson, A. M. *J. Am. Chem. Soc.* **1981**, *103*, 3559.
(10) Golding, B. T.; Gainsford, G. J.; Herlt, A. J.; Sargeson, A. M. *Tetrahedron* **1976**, *32*, 389; *Angew. Chem., Int. Ed. Engl.* **1975**, *87*, 523.
(11) Creaser, I. I.; Geue, R. J.; Harrowfield, J. MacB.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016.
(12) Geue, R. J.; Hambley, T. W.; Harrowfield, J. MacB.; Sargeson, A. M.; Snow, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 5478.

least one primary amino group, the systems chosen for this initial work were such as to provide reactants and products closely related to multidentate amine complexes of cobalt(III) where problems of stereoisomerism have been elucidated.[18-23] In the current work structural relationships for imine and amine products have been substantiated by two crystal structure determinations and some molecular mechanics calculations.[24,25] Kinetic studies of the intramolecular cyclizations leading to imine complex formation and of chloride substitution in both imine and amine complexes have also been carried out to establish the efficiency of the synthetic routes and to explore features of regio- and stereospecificity in the reactions.

### Experimental Section

**Instrumentation.** Spectrophotometric rate data and visible spectra were collected by using Cary 16 K and Varian 118C recording spectrophotometers, respectively. A hand-operated stopped-flow reactor was used to initiate reactions and allowed rates corresponding to half-lives ≥1 s to be monitored. The 100-MHz $^1H$ NMR spectra were recorded on a JEOL JNM "Minimar" spectrometer, using sodium 2,2-dimethyl-2-silapentanesulfonate as an internal reference. pH measurements were made with a Radiometer PHM 26 instrument standardized with phthalate, phosphate, and borate buffers. Infrared spectra were recorded by the KBr disk technique on a Perkin-Elmer 457 spectrometer. All evaporations were carried out in Büchi rotary evaporators at $\sim$20 Torr.

**Analyses and Syntheses.** Microanalyses were performed by the Microanalytical Unit of the Research School of Chemistry, Australian National University.

Bio-Rad Analytical Grade Dowex 50W-X2, 200–400 mesh, and SP Sephadex C25 resins were used for ion-exchange chromatographic separations. Cobalt analyses on ion-exchange eluates were performed by atomic absorption spectrophotometry.

Unless otherwise specified, all reagents used were analytical grade chemicals and were used without purification. Chloroacetone (Pfalz and Bauer), obtained as a deep purple liquid, was purified by distillation from $CaCO_3$ at atmospheric pressure and was stored under nitrogen below 5 °C. Laboratory reagent grade aminoacetaldehyde diethylacetal (Aldrich) and 2-amino-1-phenylethanol (Aldrich) were used as received. Tris(2-aminoethyl)amine hydrochloride (tren·3HCl),[26] $[Co(tren)Cl_2]Cl$,[27] $\alpha$-$[Co(trien)Cl_2]Cl$,[18,28] and $\beta$-$p$-$\Delta(R)$,$\Lambda(S)$-$[Co(trien)Cl_2]Cl$[18], were prepared by literature methods.

**Phthalimidoacetone, $C_6H_4CO(CO)NCH_2COCH_3$.** Potassium phthalimide (216 g, 1.17 mol) and *m*-xylene (290 mL) in a 1-L 3-neck round-bottomed flask fitted with a Teflon paddle stirrer and reflux condenser were stirred under a nitrogen atmosphere. Chloroacetone (133 g, 1.45 mol) was added, and the flask was immersed in an oil bath, the temperature of which was maintained at 125–130 °C for 2 h. After the reaction was cooled to 25 °C, the *m*-xylene was distilled off under vacuum. Water (300 mL) was added, and after the solid residue was broken up, so was dichloromethane (300 mL). After thorough agitation, the contents were transferred to a 1-L separating funnel. The aqueous layer was extracted twice more with dichloromethane (300 mL). The extracts were combined in a 2-L conical flask and were boiled with decolorizing charcoal ($\sim$6 g) for 10 min. The mixture was filtered through a "HYFLO" filter aid and the filtrate reduced to dryness in a rotary evaporator. The crude product was dissolved in ethanol (550 mL) by heating at $\sim$80 °C. After the addition of boiling water (500 mL), the mixture was rapidly filtered through a preheated porosity 3 sintered-glass funnel and the filtrate allowed to cool slowly to near 25 °C and then to $\sim$0 °C in an ice bath. Phthalimidoacetone crystallized as pale yellow platelets, and these were collected by filtration, washed twice with water and air-dried. Yield: 185 g (78%).

**2-(Phthalimidomethyl)-2-methyl-1,3-dioxolane.** Phthalimidoacetone (185 g) was placed in a 2-L round-bottomed flask, and dry benzene (930 mL) and ethane-1,2-diol (114 g) were added, followed by methanesulfonic acid (4.64 g). The mixture was gently refluxed, and the water evolved during the ketalization was collected with a Dean–Stark trap. After 16 h, when no more water evolution was observed (theoretical volume 16.4 mL), the reaction mixture was cooled to 25 °C. The reaction mixture was extracted twice with water (100 mL) to remove the excess diol, and then three times with 5% $Na_2CO_3$ solution (100 mL). The benzene phase was dried for 1 h with anhydrous sodium sulfate and the benzene then removed on a rotary evaporator. The solid residue was recrystallized by dissolution in the minimum volume of methanol at 80 °C, filtering, and then cooling the filtrate for a few hours at ca. 5 °C. The cream-colored crystals that separated were collected and air-dried. Yield: 149 g (66%).

**2-Methyl-2-(aminomethyl)-1,3-dioxolane.** Hydroxylamine hydrochloride (32.5 g, 0.47 mol) was placed in a 2-L round-bottomed flask fitted with a reflux condenser, drying tube, and stirrer. Ethanol (740 mL) was added; the flask was heated at reflux to dissolve the hydroxylamine hydrochloride and then cooled to $\sim$20 °C. Sodium methoxide (21.6 g of Na in 220 mL of methanol, 0.94 mol) was added, and the contents were stirred while the flask was cooled in an ice bath. 2-(Phthalimidomethyl)-2-methyl-1,3-dioxolane (33.6 g, 0.14 mol) was dissolved in ethanol (300 mL) by gentle warming, the solution was added to the flask, and the reaction mixture was stirred for 16 h at –25 °C under a dry nitrogen atmosphere. The final solution was filtered through "HYFLO", and the gelatinous residue was washed four times with ether (200-mL portions) on the filter. The combined filtrates were reduced to $\sim$100 mL on a rotary evaporator (temperature <40 °C). The residual syrup was suspended in ether (200 mL), filtered as above, and then

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(13) Harrowfield, J. MacB.; Sargeson, A. M.; Springborg, J.; Snow, M. R.; Taylor, D. *Inorg. Chem.* **1983**, *22*, 186.

(14) Buckingham, D. A.; Clark, C. R.; Foxman, B. R.; Gainsford, G. J.; Sargeson, A. M.; Wein, M.; Zanella, A. *Inorg. Chem.* **1982**, *21*, 1986.

(15) Many other important applications of cobalt(III) complexes have been investigated by others. See, for example: Buckingham, D. A.; Clark, C. R.; Deva, M. M.; Tasker, R. F. *Inorg. Chem.* **1983**, *22*, 2754 and references therein.

(16) (a) Patai, S., Ed. *The Chemistry of the Carbon-Nitrogen Double Bond*; Interscience: New York, 1970. (b) Diebler, H.; Thorneley, R. N. F. *J. Am. Chem. Soc.* **1973**, *95*, 896 and references therein. (c) Sayer, J. M.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 464.

(17) Uncoordinated imines are, of course, readily reduced also (see ref 16a) and are presumably involved in the syntheses of amine ligands such as those formed from pyridine-2-carboxaldehyde and diamines—see: Bosnich, B.; Kneen, W. R. *Inorg. Chem.* **1970**, *9*, 2191. Goodwin, H. A.; Lions, F. *J. Am. Chem. Soc.* **1960**, *82*, 5021.

(18) Sargeson, A. M.; Searle, G. H. *Inorg. Chem.* **1965**, *4*, 45; **1967**, *6*, 787.

(19) Buckingham, D. A.; Marzilli, P. A.; Sargeson, A. M. *Inorg. Chem.* **1967**, *6*, 1032.

(20) Dwyer, M. Ph.D. Thesis, Australian National University, 1971. See also: Dwyer, M.; Maxwell, I. E. *Inorg. Chem.* **1970**, *9*, 1459.

(21) (a) Buckingham, D. A.; Marzilli, L. G. *Inorg. Chem.* **1967**, *6*, 1042. (b) Buckingham, D. A.; Foster, D. M.; Marzilli, L. G.; Sargeson, A. M. *Inorg. Chem.* **1970**, *9*, 11. (c) Buckingham, D. A.; Cresswell, P. J.; Dellaca, R. J.; Dwyer, M.; Gainsford, G. J.; Marzilli, L. G.; Maxwell, I. E.; Robinson, W. T.; Sargeson, A. M.; Turnbull, K. R. *J. Am. Chem. Soc.* **1974**, *96*, 1713. (d) Buckingham, D. A.; Dwyer, M.; Gainsford, G. J.; Ho, V. J.; Marzilli, L. G.; Robinson, W. T.; Sargeson, A. M.; Turnbull, K. R. *Inorg. Chem.* **1975**, *14*, 1739. (e) Anderson, B. F.; Bell, J. D.; Buckingham, D. A.; Cresswell, P. J.; Gainsford, G. J.; Marzilli, L. G.; Robertson, G. B.; Sargeson, A. M. *Inorg. Chem.* **1977**, *16*, 3233. See also ref 24.

(22) Snow, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 3610; *J. Chem. Soc., Dalton Trans.* **1972**, 1627 and references therein.

(23) (a) El-Awady, A. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1463; **1974**, 1264 and references therein. (b) Dash, A. C.; El-Awady, A. A.; Harris, G. M. *Inorg. Chem.* **1981**, *20*, 3160. (c) Cresswell, P. J. Ph.D. Thesis, Australian National University, 1974.

(24) Buckingham, D. A.; Sargeson, A. M. *Top. Stereochem.* **1971**, *6*, 219.

(25) Brubaker, G. R.; Johnson, D. W. *Coord. Chem. Rev.* **1984**, *53*, 1.

(26) Paoletti, P.; Ciampolini, M.; Sacconi, L. *J. Chem. Soc.* **1963**, 3589.

(27) Madan, S. K.; Reiff, W. M.; Bailar, J. C., Jr. *Inorg. Chem.* **1965**, *4*, 1366 (preparations referred to as in the Ph.D. Thesis of C. F. Liu). See also ref 32 and 33.

(28) Ligand abbreviations used throughout are as follows: en = 1,2-ethanediamine; trien = 3,6-diazaoctane-1,8-diamine; tren = 3-(2-aminoethyl)-3-azapentane-1,5-diamine; Metren = *N*-methyltren = 3-(2-aminoethyl)-3,6-diazaheptan-1-amine; trenen = 3-(2-aminoethyl)-3,6-diazaoctane-1,8-diamine; Metrenen = 3-(2-aminoethyl)-3,6-diazaoct-2-ene-1,8-diamine; trenpn = 6-(2-aminoethyl)-2-methyl-3,6-diazaoctane-1,8-diamine; trenphen = 6-(2-aminoethyl)-2-phenyl-3,6-diazaoctane-1,8-diamine; trenpnim = 6-(2-aminoethyl)-2-methyl-3,6-diazaoct-2-ene-1,8-diamine; trenphenim = 6-(2-aminoethyl)-2-phenyl-3,6-diazaoct-2-ene-1,8-diamine; trenphenol = 6-(2-aminoethyl)-2-hydroxy-2-phenyl-3,6-diazaoctane-1,8-diamine; trenenol = 3-(2-aminoethyl)-2-hydroxy-3,6-diazaoctane-1,8-diamine; trenenone = 3-(2-aminoethyl)-2-oxo-3,6-diazaoctane-1,8-diamine; trenpnol = 3-(2-aminoethyl)-7-methyl-7-hydroxy-3,6-diazaocane-1,8-diamine; tetraen = 3,6,9-triazaundecane-1,11-diamine; tetraenim = 3,6,9-triazaundec-2-ene-1,11-diamine; Metetraen = 2-methyl-3,6,9-triazaundecane-1,11-diamine; Metetraenim = 2-methyl-3,6,9-triazaundec-2-ene-1,11-diamine. $p$ = substituent of highest priority trans to a $-NH_2$ site; $s$ = trans to a $-NH-$ site; $i$ = trans to imine N; $t$ = trans to tertiary N. $\alpha$ and $\beta$ define the orientation of the quadridentate trien about the metal ion as shown in structures **2** and **3**. $R$ and $S$ are the configurations about the uniquely bound secondary-N centers. $\beta$-$p$-$\Delta(S)$, $\beta$-$p$-$\Delta(R)$. The remaining secondary-N chirality is decided by the orientation of the chelate. $\alpha\beta$, $\alpha\alpha$, and $\beta$ trans define the orientation of the quinquedentate tetraen ligand about the metal ion by using the components of the trien nomenclature as indicated, for example, by structures **5** and **6**.

passed through a "Florisil" column (length 15 cm, diameter 2 cm). The column was eluted with ether (100 mL) and the ether then stripped from the combined column effluence and eluate. The residue, a pale yellow oil, was transferred to a 50-mL Claisen flask fitted with a short Vigreux column and distilled under a nitrogen atmosphere at 18 Torr. The fraction boiling below 50 °C was mainly ethanol. The pure product boiled at 59–61 °C. $^1H$ NMR $\delta$ in ppm from internal $(CH_3)_4Si$): 1.24 (sharp singlet, $-CH_3$) superimposed on 1.3 (broad, $-NH_2$), 2.71, 2.63, 2.55 (triplet, $-CH_2-$ split by $NH_2$), 3.97 (sharp singlet, ketal $CH_2-CH_2$).

***p*-[Co(tren){NH$_2$CH$_2$CH(OH)$_2$}Cl]Cl(ClO$_4$).** $H_2NCH_2CH(OC_2H_5)_2$ (1.5 g) was added to a solution of $[Co(tren)Cl_2]ClO_4$ (3.8 g) in dimethyl sulfoxide (40 mL). The mixture was stirred for 2 h at 25 °C as a color change from violet to deep red occurred. Addition of ethanol and ether precipitated the complex as an oil, which was solidified by trituration with ethanol/ether (1:1). The red solid was dissolved in HCl (1 mol $L^{-1}$, 20 mL), and the solution stood 2 h at 25 °C to allow for acetal hydrolysis (monitored by $^1H$ NMR). Addition of $HClO_4$ (70%, 5 mL) and ice cooling resulted in the deposition of red crystals, which were collected and washed with ethanol and ether and stored at 0–5 °C. Characterization of this complex has been reported previously.[6] Ion-exchange chromatography also indicated that in both steps the isolated material was the sole reaction product.

***p*-[Co(tren)(NH$_2$CH$_2$(CH$_3$)COCH$_2$CH$_2$O)Cl](ClO$_4$)$_2$.** 2-(Aminomethyl)-2-methyl-1,3-dioxolane (6 g, 20% excess) was added to a suspension of $[Co(tren)Cl_2]Cl$ (13.5 g) in methanol (1 L). The mixture was heated at reflux for 2 h, in which time most of the violet reactant complex dissolved to give a red solution. This was filtered to remove unreacted $[Co(tren)Cl_2]Cl$ (2.2 g) and the filtrate taken to dryness on the rotary evaporator. The red residue was dissolved in water (500 mL) and filtered, and the complex was precipitated by the addition of $NaClO_4$ (60 g). The red, platelike crystals that deposited were collected and washed with ethanol followed by ether. Yield: 17.1 g (85%). Anal. Calcd for $CoC_{11}H_{29}N_5Cl_3O_{10}$: Co, 10.58; C, 23.72; H, 5.25; N, 12.63; Cl, 19.09. Found: Co, 10.6; C, 23.3; H, 5.4; N, 12.7; Cl, 19.2. $^1H$ NMR in $D_2O$: $\delta$ 1.39 (s, $CH_3$), 2.6–3.4 (m, $CH_2N$), 4.10 (s, $CH_2O$) after N deuteriation. $^1H$ NMR in DMSO-$d_6$: $\delta$ 1.67 (s, $CH_3$), 2.8–4.2 (m, $CH_2N$), 4.38 (s, $CH_2O$), 5.15 (br s, tren $NH_2$), 5.80 (br s, ketal $NH_2$). Absorption spectrum in dilute HCl ($\lambda_{max} - \epsilon_{max}$): 509 nm, 108 $M^{-1}$ $cm^{-1}$; 369 nm, 115 $M^{-1}$ $cm^{-1}$.

***p*-[Co(tren)(NH$_2$CH$_2$COCH$_3$)Cl](ClO$_4$)$_2$.** *p*-$[Co(tren)(NH_2CH_2(CH_3)COCH_2CH_2O)](ClO_4)_2$ (6 g) was dissolved in 1 mol $L^{-1}$ HCl (500 mL) at 45 °C, and the solution was allowed to stand at 25 °C for 10 h. If was then taken to dryness on a rotary evaporator, the residue dissolved in 0.05 $mol^{-1}$ $HClO_4$ (35 mL), and 70% $HClO_4$ (25 mL) added slowly with continuous stirring. The red-violet crystals that deposited on cooling in ice were collected and washed with ethanol followed by ether and stored at 0–5° °C. Yield: 4.6 g (84%). Anal. Calcd for $CoC_9H_{25}N_5Cl_3O_9$: Co, 11.50; Cu, 21.09; H, 4.92; N, 13.66; Cl, 20.75. Found: Co, 11.4; C, 20.9; H, 4.8; N, 13.5; Cl, 20.9. $^1H$ NMR in 1 mol $L^{-1}$ DCl: $\delta$ 2.26 (s, $CH_3$), 2.7–4.1 (m, $CH_2$), 4.7 (br s, $NH_2$ trans to Cl), 4.95 (br s, $NH_2$ trans to tren $NH_2$), 5.2 (br s, $NH_2$ of aminoacetone). Absorption spectrum in dilute HCl ($\lambda_{max}$, $\epsilon_{max}$): 513 nm, 103 $M^{-1}$ $cm^{-1}$; 370 me, 113 $M^{-1}$ $cm^{-1}$.

***i*-[Co(trenpnim)Cl](ClO$_4$)$_2$.** *p*-$[Co(tren)(NH_2CH_2COCH_3)Cl](ClO_4)_2$ (2 g) was dissolved in water (40 mL), and the pH was adjusted to ~6.5 by the addition of $10^{-3}$ mol $L^{-1}$ NaOH. Following the rapid color change from red to orange, 12 mol $L^{-1}$ HCl (10 mL) was added and the solution was evaporated to dryness. The red residue was dissolved in water (100 mL), and the complex was sorbed on cation-exchange resin (length 10 cm, diameter 3 cm) and eluted with 1 mol $L^{-1}$ HCl. Only one (red) band was observed, and its eluate was reduced to dryness in a Büchi evaporator. The residue was dissolved in water (40 mL) and 70% $HClO_4$ (20 mL) was slowly added. After the solution was cooled to 5 °C, the red platelike crystals were collected and washed with ethanol and then ether. Yield: 1.8 g (93%). Anal. Calcd for $CoC_9H_{23}N_5Cl_3O_8$: Co, 11.91; C, 21.86; H, 4.69; N, 14.61; Cl, 21.50. Found: Co, 11.7; C, 22.0; H, 4.7; N, 13.8; Cl, 21.6. $^1H$ NMR in dilute $D_2SO_4$: $\delta$ 2.30 (s, $CH_3$), 2.95–4.45 (m, $CH_2$), 5.0 (br s, mutually trans $NH_2$), 5.5 (br s, $NH_2$ trans to tertiary N). Absorption spectrum in dilute HCl ($\lambda_{max}$, $\epsilon_{max}$): 496 nm, 180 $M^{-1}$ $cm^{-1}$; 358 nm, 185 $M^{-1}$ $cm^{-1}$.

***s*-(*SR,RS*)-[Co(trenpn)Cl](ClO$_4$)$_2$.** Excess $NaBH_4$ (0.1 g) was added to a solution of *i*-$[Co(trenpnim)Cl](ClO_4)_2$ (0.5 g) in water (25 mL) and the mixture stirred vigorously for 10 s. The solution was then rapidly absorbed (under suction) on $Na^+$ form Dowex 50W-X2 cation-exchange resin and the resin bed subsequently washed well with water. (Prolonged contact with $BH_4^-$ solution results in reduction of Co(III) to Co(II), and this process is greatly accelerated by acid.) Elution with HCl (1–3 mol $L^{-1}$) removed three components: band 1, $Co^{2+}(aq)$, was discarded but bands 2 (violet) and 3 (orange) were collected and evaporated to dryness. The complex in band 3 underwent some reaction (anation) during evaporation to give violet material chromatographically identical with that in band 2. Hence, the residues from bands 2 and 3 were combined, dissolved in water (20 mL), mixed with concentrated HCl (10 mL) and evaporated to dryness at 80 °C. The then violet-red residue was dissolved in water (20 mL) and mixed with $HClO_4$ (70%, 10 mL) and the solution cooled on ice to cause deposition of violet-red, needlelike crystals. These were collected and washed with ethanol and ether. Yield: 0.43 g (86%). Anal. Calcd for $CoC_9H_{25}N_5Cl_3O_8$: Co, 11.87; C, 21.77; H, 5.07; N, 14.10; Cl, 21.42. Found: Co, 11.9; C, 21.5; H, 5.2; N, 14.0; Cl, 21.5. $^1H$ NMR in dilute DCl: $\delta$ 1.31, 1.37 (d, $CH_3$), 2.9–4.2 (m, $CH_2$), 4.9 (br s, mutually trans $NH_2$), 5.4 (br s, $NH_2$ trans to tertiary amine), 6.1 (s, NH trans to Cl). Absorption spectrum in dilute HCl ($\lambda_{max}$, $\epsilon_{max}$): 512 nm, 148 $M^{-1}$ $cm^{-1}$; 367 nm, 136 $M^{-1}$ $cm^{-1}$.

***p*-[Co(tren)(NH$_2$CH$_2$CH(C$_6$H$_5$)OH)Cl](ClO$_4$)$_2$·0.5C$_2$H$_5$OH.** $[Co(tren)Cl_2]Cl$ (10 g) was added to a solution of 2-amino-1-phenylethanol (7.1 g, 60% excess) in methanol (1 L) and the mixture heated at reflux for 1 h, in which time most of the reactant complex dissolved to give an orange-red solution. Undissolved complex was filtered out and the filtrate acidified with HCl (12 mol $L^{-1}$, 100 mL) before being evaporated to dryness. The red-violet residue was dissolved in water and absorbed on $H^+$ form Dowex 50W-X2 cation-exchange resin. Elution with HCl (1–5 mol $L^{-1}$) separated three components. Band 1 (violet, removed with 1 mol $L^{-1}$ HCl) was found to be $[Co(tren)(OH_2)Cl]^{2+}$; band 2 (red-orange, removed with 3 mol $L^{-1}$ HCl) was taken to dryness and the red residue crystallized from water (100 mL) and ethanol (50 mL) by addition of $NaClO_4\cdot H_2O$ (30 g) and $HClO_4$ (70%, 2 mL). The red, needlelike crystals that deposited at 25 °C were washed with 2-propanol and ether before drying (yield 8 g). Band 3 (orange, very slowly eluted by 5 mol $L^{-1}$) appeared to be a bis(amino alcohol) species but was not further characterized. Data for band 2 are as follows. Anal. Calcd for $CoC_{14}H_{29}N_5Cl_3O_9\cdot{}^1/_2C_2H_5OH$: Co, 9.83; C, 30.04; H, 5.38; N, 11.68; Cl, 17.73. Found: Co, 9.6; C, 29.9; H, 5.4; N, 11.5; Cl, 17.9. $^1H$ NMR in dilute DCl: $\delta$ 2.7–4.1 (m, $CH_2$), 4.5 (br s, $NH_2$ of amino alcohol), 5.0 (br s, mutually trans $NH_2$), 5.3 (br s, $NH_2$ trans to Cl), 7.44 (s, $C_6H_5$). Absorption spectrum in dilute HCl ($\lambda_{max}$, $\epsilon_{max}$): 512 nm, 104 $M^{-1}$ $cm^{-1}$; 369 nm, 124 $M^{-1}$ $cm^{-1}$.

***p*-[Co(tren)(H$_2$NCH$_2$COC$_6$H$_5$)Cl](ClO$_4$)$_2$·H$_2$O.** A solution of $Na_2Cr_2O_7\cdot 2H_2O$ (8 g) in water (50 mL) was slowly added to a solution of *p*-$[Co(tren)(H_2NCH_2CH(C_6H_5)OH)Cl](ClO_4)_2\cdot{}^1/_2C_2H_5OH$ (6 g) in 1 mol $L^{-1}$ $H_2SO_4$ (500 mL) and the mixture stirred at 25 °C for 48 h. The final solution was diluted to a volume of 1.5 L and absorbed on $H^+$ form Dowex 50W-X2 cation-exchange resin. Elution with 1 mol $L^{-1}$ HCl removed a violet Cr(III) species, which was discarded. Subsequent elution with 3 mol $L^{-1}$ HCl removed a single red Co(III) species, which was isolated by taking the eluate to dryness, dissolving the residue in HCl (0.1 mol $L^{-1}$, 400 mL), and adding $HClO_4$ (70%, 10 mL). The red-violet crystals, which immediately deposited, were collected, washed with 2-propanol followed by ether, and stored at 0–5 °C. Yield: 4.5 g (75%). Anal. Calcd for $CoC_{14}H_{27}N_5Cl_3O_9\cdot H_2O$: Co, 9.4; C, 28.37; H, 4.93; N, 11.82; Cl, 17.95. Found: Co, 10.0; C, 28.3; H, 4.8; N, 11.7; Cl, 18.0. $^1H$ NMR in DMSO-$d_6$: $\delta$ 2.6–3.9 (m, $CH_2$), 4.10–4.30 (m, $CH_2$ of aminoacetophenone), 4.86 (br s, mutually trans $NH_2$), 5.16 (br s, $NH_2$), 5.47 (br s, $NH_2$), 7.6–8.2 (m, $C_6H_5$). Absorption spectrum in dilute HCl ($\lambda_{max}$, $\epsilon_{max}$): 511 nm, 105 $M^{-1}$ $cm^{-1}$; 368 nm, 121 $M^{-1}$ $cm^{-1}$. IR: $\nu_{C=O}$ at 1709 $cm^{-1}$.

***s*-[Co(trenphenol)Cl](ClO$_4$)$_2$·$^1/_2$H$_2$O.** *p*-$[Co(tren)(H_2NCH_2COC_6H_5)Cl](ClO_4)_2\cdot H_2O$ (0.4 g) was dissolved in dilute HCl (100 mL, pH 1.5, 25 °C) and the pH of the stirred solution raised to 5.0 by the dropwise addition of aqueous pyridine (0.1 mol $L^{-1}$). The solution was kept at this pH for 140 s; then reaction was quenched by the addition of $HClO_4$ (70%, 30 mL). After dilution to 1 L, this final solution was absorbed on $H^+$ form Dowex 50W-X2 cation-exchange resin and the column washed with 1 mol $M^{-1}$ HCl (200 mL) to remove pyridinium ions. The violet-red cobalt complex was then eluted as a single band with 5 mol $L^{-1}$ HCl and the eluate taken to dryness on the rotary evaporator. The residue was dissolved in dilute $HClO_4$ (0.1 mol $L^{-1}$, 25 mL) and filtered and the complex crystallized by the addition of $NaClO_4\cdot H_2O$ (15 g) in water (20 mL). The red-violet solid was collected and washed with 2-propanol and then ether and stored at 0–5 °C. Yield: 0.30 g. Anal. Calcd for $CoC_{14}H_{27}N_5Cl_3O_9\cdot{}^1/_2H_2O$: Co, 10.10; C, 28.81; H, 4.83; N, 11.99; Cl, 18.22. Found: Co, 10.1; C, 28.9; H, 4.7; N, 11.9; Cl, 18.3. $^1H$ NMR in DMSO-$d_6$: $\delta$ 2.6–4.0 (m, $CH_2$ and CH), 4.09–4.30 (m, $CH_2$ adjacent to carbinolamine moiety), 4.55 (br s), 4.84 (br s), 5.18 (br s), 5.50 (br s) ($NH_2$ groups), 5.90 (br s, $NH_2$ trans to Cl), 7.60–8.20 (m, $C_6H_5$), 7.68 (s, OH, shifted by addition of $D_2SO_4$). Absorption spectrum in 1 mol $L^{-1}$ HCl ($\lambda_{max}$, $\epsilon_{max}$): 504 nm, 130 $M^{-1}$ $cm^{-1}$; 362 nm, 156 $M^{-1}$ $cm^{-1}$.

***i*-[Co(trenphenim)Cl](ClO$_4$)$_2$·H$_2$O.** *p*-$[Co(tren)(H_2NCH_2COC_6H_5)Cl](ClO_4)_2\cdot H_2O$ (2 g) was dissolved in water (50 mL) and pyridine (3 mL) added. A rapid color change from red to orange was observed.

$HClO_4$ (70%, 15 mL) was slowly added, and the needlelike, orange-red crystals that deposited were collected and washed with 2-propanol followed by ether. Yield: 1.9 g (95%). Anal. Calcd for $CoC_{14}H_{25}N_5Cl_3O_9\cdot H_2O$: Co, 10.25; C, 29.26; H, 4.74; N, 12.19; Cl, 18.51. Found: Co, 10.5; C, 29.3; H, 4.9; N, 12.10; Cl, 18.4. $^1H$ NMR in dilute DCl: δ 3.0–4.3 (m, $CH_2$), 4.8 (m, $CH_2$ on imine C), 5.1 (br s), 5.4 (br s), 5.8 (br s) ($NH_2$ resonances), 7.65 (s, $C_6H_5$). Absorption spectrum in dilute HCl ($\lambda_{max}$, $\epsilon_{max}$): 497 nm, 184 $M^{-1}$ $cm^{-1}$; 352 nm, 280 $M^{-1}$ $cm^{-1}$.

***s*-[Co(trenphen)Cl]$(ClO_4)_2\cdot H_2O$.** $NaBH_4$ (1 g, large excess) was dissolved in a solution of [Co(trenphenim)Cl]$(ClO_4)_2\cdot H_2O$ (1 g) in water (200 mL) adjusted to pH 8 by addition of $Na_2CO_3/NaHCO_3$ buffer. After vigorous stirring for 10 s, the solution was absorbed on $Na^+$ form Dowex 50W-X2 cation-exchange resin and the resin column then washed thoroughly with water (to remove all excess $BH_4^-$). The column was eluted with 1 mol $L^{-1}$ HCl to remove $Na^+$ and 6 mol $L^{-1}$ HCl to remove the Co(III) complexes. The second eluate fraction was evaporated to dryness on the steam bath (to ensure anation of aqua species) and the red-violet residue dissolved in water (50 mL), filtered, and mixed with a solution of $NaClO_4$ (15 g) and $HClO_4$ (70%, 5 mL) in water (15 mL). After the mixture was cooled on ice, the lustrous, red-violet needles that precipitated were collected and washed with 2-propanol and then ether. Yield: 0.85 g (85%). Anal. Calcd for $CoC_{14}H_{27}N_5Cl_3O_8\cdot H_2O$: Co, 10.22; C, 29.16; H, 5.07; N, 12.14; Cl, 18.44. Found: Co, 10.0; C, 29.4; H, 4.9; N, 11.9; Cl, 18.4. $^1H$ NMR in dilute DCl: δ 2.4–4.2 (m, $CH_2$ and CH), 4.2–4.5 (m, $CH_2$ adjacent to $CHC_6H_5$), 5.1 (br s, mutually trans $NH_2$), 5.6 (br s, $NH_2$ trans to tertiary N), 6.0 (br s, NH trans to Cl), 7.43–7.75 (m, $C_6H_5$). Absorption spectrum in dilute HCl ($\lambda_{max}$, $\epsilon_{max}$): 514 nm, 155 $M^{-1}$ $cm^{-1}$; 365 nm, 146 $M^{-1}$ $cm^{-1}$.

***β-p*-Δ(*R*),Λ(*S*)-[Co(trien)$(H_2NCH_2CH(OCH_2CH_3)_2)$Cl]$Br_2\cdot{}^1/_2H_2O$.** Finely ground *α*-[Co(trien)$Cl_2$]Cl (21.7 g) was added to a solution of $H_2NCH_2CH(OCH_2CH_3)_2$ (11.3 g, 30% excess) in methanol (750 mL) and the mixture heated at reflux for 2 h, in which time nearly all the reactant complex dissolved to give a deep red solution. This was cooled to 25 °C, filtered, and then reduced in volume to 200 mL. The red precipitate that formed was collected and combined with further material deposited when the filtrate volume was reduced to 80 mL. Further evaporation gave only an intractable orange-red gum. The crude red chloride salt was converted to the bromide by dissolution in water (75 mL/10 g) and addition of a large excess of NaBr. Rapid precipitation was necessary to minimize losses due to aquation. Yield: 8 g (22%). The anhydrous perchlorate salt may be obtained by substituting $NaClO_4$ for NaBr. Anal. Calcd for $CoC_{12}H_{33}N_5O_2ClBr_2\cdot{}^1/_2H_2O$: Co, 10.86; C, 26.56; H, 6.32; N, 12.91. Found: Co, 11.1; C, 26.7; H, 6.3; N, 12.9. Calcd for $CoC_{12}H_{31}N_5Cl_3O_9$: Co, 10.29; C, 25.17; H, 5.81; N, 12.23; Cl, 18.57. Found: Co, 10.3; C, 25.2; H, 5.7; N, 12.1; Cl, 18.8. $^1H$ NMR in dilute DCl: δ 1.16, 1.23, 1.28 (t, $CH_3$), 3.61, 3.69, 3.76, 3.82 and 3.68, 3.74, 3.81, 3.86 (AB quartets of diastereotopic $CH_2$ groups of the acetal moiety), 2.6–3.9 (m, $CH_2N$ groups), 4.15 (br s, $NH_2$ of acetal superimposed on trien $NH_2$ trans to Cl), 4.81, 4.86, 4.91 (t, CH of acetal), 4.75, 5.35 (br s, $NH_2$ groups cis to Cl), 6.60 (br s, planar NH), 7.05 (br s, angular NH). Absorption spectrum in dilute HCl ($\lambda_{max}$, $\epsilon_{max}$): 481 nm, 91 $M^{-1}$ $cm^{-1}$; 364 nm, 100 $M^{-1}$ $cm^{-1}$.

***β-p*-(*RR*)(*SS*)-[Co(trien)$(H_2NCH_2CH(OH)_2)$Cl]$Cl_2$.** *β-p*-(*RR*)-(*SS*)-[Co(trien)$(H_2NCH_2CH(OCH_2CH_3)_2)$Cl]$Br_2$ (5 g) was dissolved in HCl (1 mol $L^{-1}$, 200 mL) and the solution kept at 25 °C for 16 h. The volume was then reduced to 50 mL on the rotary evaporator (at <35 °C) and acetone (~200 mL) added until the solution became turbid. Cooling to 0 °C produced a red powder, which was collected and washed with acetone and ether. This solid was not stable to storage at 20 °C and was kept at 0 °C until usage as soon as possible in further preparations. A small portion was recrystallized for analysis by addition of acetone to its concentrated solution in dilute HCl, but a mixed chloride/bromide salt appeared to be obtained. Anal. Calcd for $CoC_8H_{25}N_5O_2Cl_{2.5}Br_{0.5}$: Co, 14.34; C, 23.39; H, 6.13; N, 17.05; Cl, 21.33. Found: Co, 14.0; C, 23.6; H, 6.3; N, 17.0; Cl, 21.6. $^1H$ NMR in dilute DCl: δ 2.6–3.9 (m, $CH_2$ of trien and aminoacetaldehyde), 4.35 (br s, $NH_2$ of aminoacetaldehyde and of trien trans to Cl), 4.74 (br s), 5.45 (br s) ($NH_2$ groups of trien cis to Cl), 5.27, 5.33, 5.38 (t, CH of aminoacetaldehyde), 6.70 (br s, planar NH), 7.02 (br s, angular NH). Absorption spectrum in dilute HCl ($\lambda_{max}$, $\epsilon_{max}$): 481 nm, 90 $M^{-1}$ $cm^{-1}$; 365 nm, 102 $M^{-1}$ $cm^{-1}$. The IR spectrum showed no evidence of $\nu_{C=O}$, consistent with the indications from the $^1H$ NMR spectrum that the aminoacetaldehyde was fully hydrated.

***αβ-i*-[Co(tetraenim)Cl]$(ClO_4)_2$.** The pH of a solution of crude *β-p*-(*RR*)(*SS*)-[Co(trien)$(H_2NCH_2CH(OH)_2)$Cl]$Cl_{1.5}Br_{0.5}$ (3.2 g) in water (60 mL) was maintained at 6.2 ± 0.1 for 3 h (at 25 °C) by dropwise addition of aqueous pyridine (0.1 mol $L^{-1}$). The solution changed color from red to a deep orange over this period. It was then diluted to 250 mL with water and absorbed on $H^+$ form Dowex 50W-X2 cation-exchange resin. Elution with 1 mol $L^{-1}$ HCl removed a minor red component, which was crystallized as its perchlorate salt (using $HClO_4$) after the eluate had been taken to dryness and the residue dissolved in the minimum volume of dilute HCl. Elution with 3 mol $L^{-1}$ HCl removed a major orange component and left some brown decomposition product strongly adhering to the top of the resin column. This eluate was evaporated to dryness at 80 °C to anate the aqua ion generated in the reaction, and the red-orange residue was dissolved in 0.1 mol $L^{-1}$ HCl (40 mL) and crystallized by the addition of $HClO_4$ (70%, 10 mL). Spectroscopically and chromatographically the two samples of red perchlorate salts appeared identical and hence were combined. Total yield 1.5 g. Anal. Calcd for $CoC_8H_{21}N_5Cl_3O_8$: Co, 12.26; C, 20.00; H, 4.41; N, 14.57; Cl, 22.13. Found: Co, 12.6; C, 19.9; H, 4.2; N, 14.4; Cl, 22.2. $^1H$ NMR in dilute DCl: δ 2.26–3.7 (m, $CH_2$ groups, remote from imine), 4.1–4.6 (m, $CH_2$ groups adjacent to imine moiety), 5.18 (br s, $NH_2$ trans to planar NH), 5.50, 5.80 (br d, $NH_2$ trans to angular NH), 6.3 (br s, planar NH), 6.5 (br s, angular NH), 8.15 (s, –CH=N). IR: $\nu_{C=N}$ 1680 $cm^{-1}$. Absorption spectrum in dilute HCl ($\lambda_{max}$, $\epsilon_{max}$): 474 nm, 127 $M^{-1}$ $cm^{-1}$; 350 nm, 128 $M^{-1}$ $cm^{-1}$.

**Reduction of *αβ-i*-[Co(tetraenim)Cl]$^{2+}$ to *αβ*-[Co(tetraen)Cl]$^{2+}$ Isomers.** *αβ-i*-[Co(tetraenim)Cl]$(ClO_4)_2$ (0.4 g) was dissolved in water (100 mL) and the pH adjusted to 7 by using dilute NaOH. $NaBH_4$ (0.2 g) was added, and after vigorous stirring for 10 s, the solution was absorbed on $Na^+$ form Dowex 50W-X2 cation-exchange resin. The resin column was washed well with water, and 1 mol $L^{-1}$ HCl was then used to elute a trace of $Co^{2+}$(aq). Orange Co(III) complexes were subsequently rapidly eluted with 4 mol $L^{-1}$ HCl and the eluate taken to dryness at 80 °C to cause $Cl^-$ anation. The red residue was dissolved in water and reabsorbed on $H^+$ form Dowex 50W-X2 resin. Elution with 1 mol $L^{-1}$ HCl then provided the two diastereoisomers: band 1 (7 ± 1%), *αβ*-Δ(*S*)Λ-(*R*)-[Co(tetraen)Cl]$^{2+}$, and band 2 (93 ± 1%), *αβ*-Δ(*R*)Λ(*S*)-[Co(tetraen)Cl]$^{2+}$ (total yield 81%).

***αβ-i*-[Co(tetraenim)$NO_2$]$ZnCl_4$.** *αβ-p*-[Co(tetraenim)Cl]$(ClO_4)_2$ (0.4 g) was dissolved in 0.1 mol $L^{-1}$ $HClO_4$ (20 mL) and $NaNO_2$ (1.6 g) added. The mixture was heated in the steam bath for 20 min to give a yellow solution, which was poured while hot into a 1:1 acetone/2-propanol mixture (150 mL) containing $ZnCl_2$ (4 g) and concentrated HCl (1 mL). When the mixture was cooled to 0 °C, the yellow product that deposited was collected and washed with acetone and ether. Yield: 0.4 g (100%). Anal. Calcd for $CoZnC_8H_{21}N_6O_2Cl_4$: Co, 11.80; C, 19.24; H, 4.24; N, 16.83; Cl, 28.39. Found: Co, 11.8; C, 19.3; H, 4.4; N, 16.5; Cl, 28.2. $^1H$ NMR in dilute DCl: δ 2.7–3.8 (m, $CH_2$ remote from imine moiety), 3.9–4.3 (m, $CH_2$ adjacent to imine moiety), 4.98 (br s, $NH_2$ trans to planar NH), 5.35 (br s), 5.60 (br s), 6.15 (br s), 6.30 (br s) (NH and $NH_2$ resonances), 8.29 (s, –CH=N). Absorption spectrum in dilute $HClO_4$ ($\lambda_{max}$, $\epsilon_{max}$): 447 nm, 236 $M^{-1}$ $cm^{-1}$; 325 nm, 2370 $M^{-1}$ $cm^{-1}$. Evaporation of a solution of this complex in 4 mol $L^{-1}$ HCl resulted in quantitative reformation of the reactant chloro complex.

**Reduction of *αβ-i*-[Co(tetraenim)$NO_2$]$^{2+}$ to *αβ*-[Co(tetraen)$NO_2$]$^{2+}$ Diastereoisomers.** [Co(tetraenim)$NO_2$]$ZnCl_4$ (0.2 g) was dissolved in water (50 mL) and the pH adjusted to 8 with 0.1 mol $L^{-1}$ NaOH. $NaBH_4$ (0.2 g) was added, and after being vigorously stirred for 20 s, the solution was absorbed on $Na^+$ form Dowex 50W-X2 resin and the resin column washed well with water. Elution with 1 mol $L^{-1}$ HCl revealed two yellow components: band 1 (35%; $\lambda_{max}$ = 459 nm, $\epsilon_{max}$ = 205 $M^{-1}$ $cm^{-1}$), *αβ*-Δ(*S*)Λ(*R*)-[Co(tetraen)$NO_2$]$^{2+}$, and band 2 (65%; $\lambda_{max}$ = 456 nm, $\epsilon_{max}$ = 196 $M^{-1}$ $cm^{-1}$), *αβ*-Δ(*R*)Λ(*S*)-[Co(tetraen)$NO_2$]$^{2+}$.

***α*-[Co(trien){$H_2NCH_2(CH_3)C(OCH_2CH_2O)$}Cl]$Br_2\cdot H_2O$.** A suspension of finely ground *β*-[Co(trien)$Cl_2$]Cl (6.5 g) in methanol (400 mL) containing $H_2NCH_2C(OCH_2CH_2O)(CH_3)$ (3.5 g, 50% excess) was heated at reflux for 15 min, in which time the reactant complex completely dissolved to give a red-violet solution. This was taken to dryness in the rotary evaporator and the residue redissolved in water (120 mL). Addition of NaBr (15 g) led to deposition of the slightly soluble bromide salt (5.5 g), though for further experiments it was preferable to isolate the more soluble perchlorate salt by substitution of $NaClO_4$ for NaBr. Anal. Calcd for $CoC_{11}H_{29}N_5O_2ClBr_2\cdot H_2O$: Co, 11.00; C, 24.67; H, 5.83; N, 13.08. Found: Co, 11.0; C, 24.5; H, 5.8; N, 13.1. Calcd for $CoC_{11}H_{29}N_5Cl_3O_{10}$: Co, 10.59; C, 23.73; H, 5.25; N, 12.58; Cl, 19.11. Found: Co, 10.6; C, 23.7; H, 5.2; N, 12.3; Cl, 19.3. $^1H$ NMR in dilute DCl: δ 1.37 (s, $CH_3$), 2.5–3.8 (m, $CH_2$ of trien and $CH_2NH_2$ of ketal), 4.11 (s, $OCH_2CH_2O$), 4.38 (br s, $NH_2$ of ketal), 5.52 (br s, $NH_2$ groups of trien), 5.80 (br s, NH trans to Cl), 6.50 (br s, NH cis to Cl). Absorption spectrum in water ($\lambda_{max}$, $\epsilon_{max}$): 532 nm, 105 $M^{-1}$ $cm^{-1}$; 364 nm, 106 $M^{-1}$ $cm^{-1}$.

***α*-[Co(trien)$(H_2NCH_2COCH_3)$Cl]$(ClO_4)_2$.** *α*-[Co(trien){$H_2NCH_2C(OCH_2CH_2O)(CH_3)$}Cl]$Br_2\cdot H_2O$ (2.5 g) was dissolved in 1 mol $L^{-1}$ HCl (100 mL) and kept at 25 °C for 20 h. The solution was then taken to dryness under vacuum, the violet residue dissolved in 0.1 mol $L^{-1}$ $HClO_4$

(35 mL), and product crystallization induced by addition of $HClO_4$ (70%, 15 mL) and cooling to 5 °C. The violet crystals were washed with ethanol and ether and stored at 0 °C as a precaution against decomposition. Yield: 2 g. Anal. Calcd for $CoC_9H_{25}N_5Cl_3O_9$: Co, 11.50; C, 21.09; H, 4.92; N, 13.66; Cl, 20.75. Found: Co, 11.6; C, 21.1; H, 4.8; N, 13.4; Cl, 20.5. $^1H$ NMR in dilute DCl: $\delta$ 2.26 (s, $CH_3$), 2.6–3.8 (m, $CH_2$), 4.40 (br s, aminoacetone $NH_2$), 5.25 (br s, $NH_2$ groups of trien), 6.18 (br s, NH trans to Cl), 6.56 (br s, NH cis to Cl). Absorption spectrum in water ($\lambda_{max}$, $\epsilon_{max}$): 534 nm, 105 $M^{-1}$ $cm^{-1}$; 365 nm, 104 $M^{-1}$ $cm^{-1}$.

***αβ-s*-[Co(Metetraenim)Cl](ClO)$_2$.** *α*-[Co(trien)($H_2NCH_2COCH_3$)Cl]($ClO_4$)$_2$ (1.0 g) was dissolved in water (70 mL) and the pH of the solution maintained at 6.0 for 30 min (at 25 °C). The orange-red solution was absorbed on $H^+$ form Dowex 50W-X2 cation-exchange resin. Elution with HCl (1–3 mol $L^{-1}$) revealed two components, red (chloro) and orange (aqua complex). The orange trailing material was spectroscopically identical with the residue from the leading red component after its HCl eluate was slowly evaporated to dryness. The combined residues were dissolved in water (35 mL) and $NaClO_4 \cdot H_2O$ added to cause deposition of red, needlelike crystals. These were collected and washed with ethanol and ether. Yield: 0.9 g (90%). Anal. Calcd for $CoC_9H_{23}N_5Cl_3O_8$: Co, 11.92; C, 21.86; H, 4.69; N, 14.16; Cl, 21.50. Found: Co, 12.0; C, 21.8; H, 4.8; N, 14.0; Cl, 21.5. $^1H$ NMR in dilute $D_2SO_4$: $\delta$ 2.43 (s, $CH_3$), 2.55–3.65 (m, $CH_2$), 4.04 (s, $=NCH_2$), 4.35, 4.42, 4.49 (m, $CH_2C=N$), 5.15 (br s, $NH_2$ trans to imine N), 5.42 (br s), 5.88 (br s) ($NH_2$ cis to imine), 6.30 (br s, NH trans to Cl), 6.55 (br s, NH cis to Cl). Absorption spectrum in dilute HCl ($\lambda_{max}$, $\epsilon_{max}$): 516 nm, 117 $M^{-1}$ $cm^{-1}$; 354 nm, 113 $M^{-1}$ $cm^{-1}$.

**Reduction of *αβ-s*-[Co(Metetraenim)Cl]$^{2+}$ to Isomers of [Co(Metetraen)Cl]$^{2+}$.** $NaBH_4$ (0.2 g) was added to a solution of *αβ-s*-[Co(Metetraenim)Cl]($ClO_4$)$_2$ (0.5 g) in water (25 mL, pH 8) and the mixture stirred well for 30 s before being rapidly absorbed on $Na^+$ from Dowex 50W-X2 cation-exchange resin. The resin column was washed well with water and eluted with 1 mol $L^{-1}$ HCl to remove $Na^+$ and a trace of $Co^{2+}$(aq). The Co(III) complexes were eluted with 4 mol $L^{-1}$ HCl and the eluate taken to dryness at 80 °C to cause anation. The red-violet residue was dissolved in water and reabsorbed on $H^+$ form Dowex 50W-X2 and elution with 1 mol $L^{-1}$ HCl used to separate three species. Band 2 proved to be unreduced reactant complex but bands 1 and 3 were the $\Lambda(S)_N(R)_C$, $\Delta(R)_N(S)_C$, and $\Lambda(R)_N(S)_C$, $\Delta(S)_N(R)_C$ diastereoisomeric pairs, respectively, of [Co(Metetraen)Cl]$^{2+}$. The eluates from fractions 1 and 3 were separately taken to dryness under vacuum and the residues crystallized as perchlorate salts by addition of $NaClO_4$ to their solutions in 0.01 mol $L^{-1}$ $HClO_4$. Anal. Calcd for $CoC_9H_{25}N_5Cl_3O_8 \cdot {}^1/_2H_2O$ (band 1; 15% yield): Co, 11.66; C, 21.38; H, 5.18; N, 13.85; Cl, 21.04. Found: Co, 11.7; C, 21.1; H, 5.2; N, 13.6; Cl, 20.9. Calcd for $CoC_9H_{25}N_5Cl_3O_8$ (band 3; 45% yield): Co, 11.87; C, 21.77; H, 5.07; N, 14.10; Cl, 21.42. Found: Co, 11.9; C, 21.9; H, 5.1; N, 14.0; Cl, 21.4. $^1H$ NMR in dilute DCl: band 1, $\delta$ 1.35, 1.41 (d, $CHCH_3$), 2.3–3.9 (m, $CH_2$ and CH), 4.62 (br s, $NH_2$ trans to planar NH), 5.55 (br s, NH trans to Cl), 5.77 (br s, $NH_2$ cis to planar NH), 6.25 (br s, planar NH and angular NH cis to Cl); band 2, $\delta$ 1.36, 1.42 (d, $CHCH_3$), 2.3–3.8 (m, $CH_2$ and CH), 4.60 (br s, $NH_2$ trans to planar NH), 5.41 (br s, $NH_2$ cis to planar NH), 6.06 (br s, NH trans to Cl), 6.52 (planar NH and angular NH cis to Cl). Absorption spectra in dilute HCl ($\lambda_{max}$, $\epsilon_{max}$): band 1, 531 nm, 106 $M^{-1}$ $cm^{-1}$; 486 nm (sh), 102 $M^{-1}$ $cm^{-1}$; 361 nm, 112 $M^{-1}$ $cm^{-1}$; band 3, 528 nm, 120 $M^{-1}$ $cm^{-1}$; 480 nm (sh), 110 $M^{-1}$ $cm^{-1}$; 363 nm, 112 $M^{-1}$ $cm^{-1}$.

***αβ-s*-[Co(Metetraenim)$NO_2$]$ZnCl_4$.** *αβ-s*-[Co(Metetraenim)Cl]($ClO_4$)$_2$ (0.3 g) was dissolved in 0.1 mol $L^{-1}$ HCl (20 mL) and $NaNO_2$ (1.0 g) added. The mixture was heated on the steam bath for 20 min and the hot orange solution then slowly poured into 2-propanol/acetone (1:1, 200 mL) containing $ZnCl_2$ (4 g) and HCl (12 mol $L^{-1}$; 2 mL). The orange-yellow powder that deposited on cooling was collected and washed with acetone and ether. Yield: 0.3 g (100%). Anal. Calcd for $CoZnC_9H_{23}N_6O_2Cl_4$: Co, 11.48; C, 21.05; H, 4.51; N, 16.37; Cl, 27.62. Found: Co, 11.2; C, 21.0; H, 4.5; N, 15.7; Cl, 27.9. Absorption spectrum in dilute HCl ($\lambda_{max}$, $\epsilon_{max}$): 448 nm, 221 $M^{-1}$ $cm^{-1}$; 322 nm, 1995 $M^{-1}$ $cm^{-1}$. Evaporation of a solution of this complex in 4 mol $L^{-1}$ HCl resulted in quantitative reformation of the reactant chloro complex.

Reduction of this nitro complex with sodium borohydride under the same conditions as described above for the chloro analogue gave closely parallel results. Thus, chromatography (Dowex 50W-X2, 1 mol $L^{-1}$ HCl) of the reaction products revealed three components, with the second eluted again being unreacted imine compound. Band 1 (47%; $\lambda_{max}$ = 460 nm, $\epsilon_{max}$ = 207 $M^{-1}$ $cm^{-1}$) was converted by HCl to the $\Lambda(S)_N(R)_C$, $\Delta(R)_N(S)_C$ chloro racemate and band 3 (11%; $\lambda_{max}$ = 457 nm, $\epsilon_{max}$ = 211 $M^{-1}$ $cm^{-1}$) to the $\Lambda(R)_N(S)_C$, $\Delta(S)_N(R)_C$ racemate.

**Rate Measurement and Analysis.** Reaction rates under a nitrogen atmosphere were monitored by fixed-wavelength spectrophotometry. Slower reactions ($t_{1/2}$ > 2 min) were followed under pH stat conditions where the reaction mixture pH was directly and continuously monitored. Faster reactions were conducted by using a simple stopped-flow reactor and buffer solutions. The pH of the reactor effluent was checked to see that it was unchanged (±0.02) from the initial buffer reading. Complexes were recovered from reaction mixtures by absorption on cation-exchange resins and the products separated by elution chromatography.

Proton exchange reactions were monitored by $^1H$ NMR spectroscopy using acetate or pyridine buffers in $D_2O$. Some approximate estimates of intramolecular cyclization rates were also based on these measurements.

Rate constants were extracted from absorbance or signal intensity vs time data by using locally written least-squares-fitting programs implemented on the Univac 1108 computer.

**Strain Energy Minimization Calculations.** Strain energy calculations were performed on the Univac 1108 computer by using the program MOL, originated by Boyd[29] and subsequently developed by Snow,[22] Maxwell,[21c] Dwyer,[20] and Gainsford.[21c] Perspective drawings were prepared by using ORTEP and a Calcomp plotter on line to a PDP-11 computer.

**Crystal Structure Determination.** Crystals of the isomers of [Co(Metetraen)Cl]($ClO_4$)$_2$ were grown by dissolving 50-mg samples in hot (80 °C) 1 mol $L^{-1}$ HCl, filtering these solutions, adding $HClO_4$ (70%, 0.2 mL), and cooling slowly. Thus, the material from band 1 (15%) of the HCl/Dowex 50W-X2 separation of *αβ-s*-[Co(Metetraenim)Cl]$^{2+}$ reduction products provided twinned rose-red tablets (isomer T), while the material from band 3 (45%) provided clusters of thin, red needles (isomer N). Unique data sets were measured at 295 K on specimens somewhat inferior with respect to both size and integrity by using Enraf-Nonius CAD-4 and Syntex $P\bar{1}$ four-circle diffractometers equipped with monochromatic Mo K$\alpha$ radiation sources ($\lambda$ = 0.7106$_9$ Å) and operating in the conventional $2\theta/\theta$ scan mode. $N$ independent reflections were obtained, $N_o$ with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement; data for the better of the two specimens were corrected for absorption (analytical correction). Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Residuals on $|F|$ at convergence are conventional and $R$ and $R'$ with statistical weights derived from $\sigma^2(I) = \sigma^2(I)_{diff} + 0.0005\sigma^4(I)_{diff}$ being used. Neutral complex scattering factors were employed;[30] computation was carried out with the XTAL program system implemented by S. R. Hall[31] on a Perkin-Elmer 3240 computer.

**Crystal Data.** Isomer N: $C_9H_{25}N_5Cl_3O_8Co$, $M_r$ = 496.6, orthorhombic, space group *Pcab* (No. 61, variant), $a$ = 30.022 (8) Å, $b$ = 12.034 (14) Å, $c$ = 10.350 (3) Å, $U$ = 3739 Å$^3$, $D_c$ ($Z$ = 8) = 1.77 g $cm^{-3}$. $F(000)$ = 2048. $\mu_{Mo}$ = 14.1 $cm^{-1}$. Specimen: 0.09 × 0.09 × 0.4 mm. $2\theta_{max}$ = 50°. $N$ = 3284, $N_o$ = 2610. $R$ = 0.069, $R'$ = 0.082.

Isomer T: $C_9H_{25}N_5Cl_3O_8Co \cdot H_2O$, $M_r$ = 514.6, triclinic, space group $P\bar{1}$ (No. 2), $a$ = 12.66 (1) Å, $b$ = 9.223 (5) Å, $c$ = 8.939 (3) Å, $\alpha$ = 79.20 (4)°, $\beta$ = 76.38 (5)°, $\gamma$ = 78.86 (5)°, $U$ = 984 Å$^3$, $D_c$ ($Z$ = 2) = 1.74 g $cm^{-3}$. $F(000)$ = 532. $\mu_{Mo}$ = 13.7 $cm^{-1}$. Specimen: 0.05 × 0.26 × 0.05 mm, $A^*_{min,max}$ = 1.07, 1.15. $2\theta_{max}$ = 45°. $N$ = 2598, $N_o$ = 1882. $R$ = 0.051, $R'$ = 0.049.

**Abnormal Features in Isomer N.** Difference maps displayed significant unusual features in the vicinity of N(10) and C(11); these were meaningfully refined, modeled as fractional carbon atoms C(01) and C(02) with isotropic thermal parameters $10^3U_{iso}$ = 24 (5), 77 (12) Å$^2$, respectively. Although the data for this specimen were inferior, the nature of the specimen makes it more reasonable to suppose the presence of a small component of another conformer, since C(01)···N(10), C(01)···C(9), C(01)···C(11), and C(01)···C(111) are 0.84 (1), 1.94 (2), 1.10 (2), and 1.80 (2) Å and C(02)···Cl(1) is 0.64 (3) Å. It would be unreasonable to suppose that this in any way invalidates the conclusion that connectivity and stereochemistry are in accord with the above assignment.

## Results and Discussion

**Complex Ion Characterization.** Although most of the complexes described herein incorporate a common $CoN_5Cl$ chromophore, their ligand field absorption spectra are quite distinct, an observation that is completely consistent with data for structurally characterized isomers in complex ion systems such as [Co(tren)($NH_3$)Cl]$^{2+}$,[32] [Co(Metren)($NH_3$)Cl]$^{2+}$,[33] [Co(tetraen)-

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(29) Boyd, R. H. *J. Chem. Phys.* **1967**, *47*, 3736.

(30) Ibers, J. A., Hamilton, W. C., Eds. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

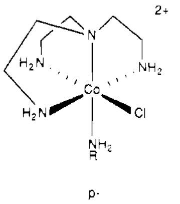
(31) Stewart, J. M., Ed. "The X-ray System—Version of March, 1976"; Technical Report TR-446; Computer Science Center, University of Maryland: College Park, MD, 1976.

**Table I.** Absorption Bands of $^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ Parentage in $\mathrm{Co^{III}N_5Cl^{2+}}$

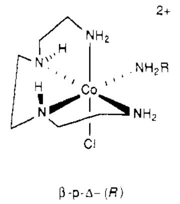
| complex | $\lambda_{max}$/nm | $\epsilon_{max}$/ $M^{-1}$ $cm^{-1}$ |
|---|---|---|
| *p*-[Co(tren)($\mathrm{H_2NCH_2COCH_2CH_2O(CH_3)}$)Cl]$^{2+}$ | 509 | 108 |
| *p*-[Co(tren)($\mathrm{H_2NCH_2COCH_3}$)Cl]$^{3+}$ | 513 | 103 |
| *p*-[Co(tren)($\mathrm{H_2NCH_2CH(OH)C_6H_5}$)Cl]$^{2+}$ | 512 | 104 |
| *p*-[Co(tren)($\mathrm{H_2NCH_2COC_6H_5}$)Cl]$^{2+}$ | 511 | 105 |
| *p*-[Co(tren){$\mathrm{H_2NCH_2CH(OH)_2}$}Cl]$^{2+}$[6] | 511 | 105 |
| *p*-[Co(tren)($\mathrm{NH_3}$)Cl]$^{2+}$[32] | 512 | 94 |
| *t*-[Co(tren)($\mathrm{NH_3}$)Cl]$^{2+}$[32] | 530 | 136 |
| *t*-[Co(Metren)($\mathrm{NH_3}$)Cl]$^{2+}$[33] | 534 | 139 |
| *t*-[Co(*N*-Metrenen)Cl]$^{2+}$[36] | 534 | 152 |
| *t*-[Co(trenenol)Cl]$^{2+}$[5c] | 531 | 147 |
| *t*-[Co(trenenone)Cl]$^{2+}$[5c] | 532 | 137 |
| *s*-[Co(trenen)Cl]$^{2+}$[35] | 512 | 151 |
| *s*-(*SR*,*RS*)- or *s*-(*SR*)-[Co(trenpn)Cl]$^{2+}$ | 512 | 148 |
| *s*-(*SR*,*RS*)- or *s*-(*SR*)-[Co(trenphen)Cl]$^{2+}$ | 514 | 155 |
| *s*-(*SS*,*RR*)- or *s*-(*SS*)-[Co(trenphenol)Cl]$^{2+}$ | 504 | 130 |
| *i*-[Co(trenenim)Cl]$^{2+}$[6] | 494 | 195 |
| *i*-[Co(trenpnim)Cl]$^{2+}$ | 496 | 180 |
| *i*-[Co(trenphenim)Cl]$^{2+}$ | 497 | 184 |
| β-*p*-Δ(*R*)-[Co(trien)($\mathrm{NH_3}$)Cl]$^{2+}$[20] | 475 | 93 |
| β-*p*-Δ(*S*)-[Co(trien)($\mathrm{NH_3}$)Cl]$^{2+}$[20] | 475 | 84 |
| β-*p*-Δ(*R*)-[Co(trien){$\mathrm{HNCH_2CH(OEt)_2}$}Cl]$^{2+}$ | 481 | 91 |
| β-*p*-Δ(*R*)-[Co(trien){$\mathrm{H_2NCH_2CH(OH)_2}$}Cl]$^{2+}$ | 481 | 90 |
| α-[Co(trien)($\mathrm{NH_3}$)Cl]$^{2+}$[20] | 530 | 95 |
| α-[Co(trien)($\mathrm{H_2NCH_2(CH_3)COCH_2CH_2O}$)Cl]$^{2+}$ | 532 | 105 |
| α-[Co(trien)($\mathrm{H_2NCH_2COCH_3}$)Cl]$^{2+}$ | 534 | 105 |
| α-[Co(trien){$\mathrm{H_2NCH_2CH(OH)_2}$}Cl]$^{2+}$[5c] | 534 | 106 |
| αβ-*i*-[Co(tetraenim)Cl]$^{2+}$ | 474 | 127 |
| αβ-*s*-[Co(Metetraenim)Cl]$^{2+}$ | 516 | 117 |
| αβ-Λ(*S*)-[Co(tetraen)Cl]$^{2+}$[22] | 532, 482 | 101, 103 |
| αβ-Λ(*R*)-[Co(tetraen)Cl]$^{2+}$[22] | 530, 490 (sh) | 110, 104 |
| αα-[Co(tetraen)Cl]$^{2+}$ | 532 | 88 |
| αβ-$(R)_N(S)_C$-[Co(Metetraen)Cl]$^{2+}$ | 531, 486 | 106, 102 |
| αβ-$(S)_N(R)_C$-[Co(Metetraen)Cl]$^{2+}$ | 528, 480 (sh) | 120, 110 |

[a] All spectra recorded in aqueous media, usually 1 mol $L^{-1}$ HCl.

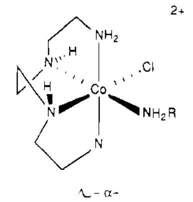
Cl]$^{2+}$,[22,23] and [Co(trien)($\mathrm{NH_3}$)Cl]$^{2+}$.[20] On the empirical basis of a close similarity in absorption spectra (Table I), therefore, all [Co(tren)($\mathrm{H_2NR}$)Cl]$^{2+}$ species isolated herein have been assigned the *p* structure (**1**) known for the "red" isomer of [Co(tren)($\mathrm{NH_3}$)Cl]$^{2+}$.[32,33] On the same basis (Table I) [Co(trien){$\mathrm{H_2NCH_2CH(OR)_2}$}Cl]$^{2+}$ (R = $\mathrm{CH_2CH_3}$, H) complexes have been assigned the β-*p*-Δ(R)-[Co(trien)($\mathrm{NH_3}$)Cl]$^{2+}$ structure (**2**)[18,19] and the [Co(trien){$\mathrm{H_2NCH_2(CH_3)COCH_2CH_2O}$}Cl]$^{2+}$ and [Co(trien)($\mathrm{H_2NCH_2COCH_3}$)Cl]$^{2+}$ complexes the α-[Co(trien)($\mathrm{NH_3}$)Cl]$^{2+}$ structure (**3**)[18,20] (and their equivalent catoptric configurations). Since removal of protecting groups from the coordinated carbonyl compounds was achieved without substitution at Co(III) or NH exchange, it is expected on the basis of the stereochemical rigidity of Co(III)–acidoamine complexes[34,35] that the coordination geometry of free and protected ligand species should be identical.



(1)

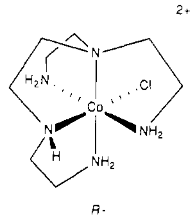


(2)

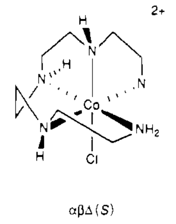


(3)

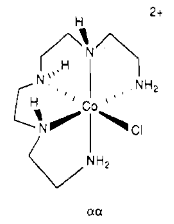
The [Co(trenpn)Cl]$^{2+}$ and [Co(trenphen)Cl]$^{2+}$ complexes have been assigned the *s*-[Co(trenen)Cl]$^{2+}$ structure (**4**), also on the basis of spectral similarity (and dissimilarity with the known structure[36] of *t*-[Co(N-Metrenen)Cl]$^{2+}$). Assignment of the same structure to [Co(trenphenol)Cl]$^{2+}$ is consistent with a considerable difference between its spectrum and that of structurally characterized *t*-[Co(trenenol)Cl]$^{2+}$.[5c] The [Co(trenpnim)Cl]$^{2+}$ and [Co(trenphenim)Cl]$^{2+}$ complexes are spectrally similar to *i*-[Co(trenenim)Cl]$^{2+}$ and may be assigned skeletal structure **4** on the basis of the fact that conversion of the chloro–tren–aminocarbonyl complexes via imines to chloro–substituted-trenen) species can be achieved without substitution and hence presumably without stereochemical change about cobalt(III). The same argument supports the assignment of structure **4** to [Co(trenphenol)Cl]$^{2+}$.



(4)



(5)



(6)

Structural assignments based on spectral data (summarized in Table I) for [Co(trien)(aminocarbonyl)Cl]$^{2+}$-derived complexes are somewhat tenuous due to the limited comparisons possible and the relatively subtle differences between known isomers.[22,23] Also, the fact that base hydrolysis of Cl$^-$ was faster than imine group reduction in [Co(tetraenim)Cl]$^{2+}$ and [Co(Metetraenim)Cl]$^{2+}$ species meant that the configurations of the finally isolated [Co(tetraen)Cl]$^{2+}$ and [Co(Metetraen)Cl]$^{2+}$ species could not be correlated with reactants (due to possible isomerization of the five-coordinate intermediates[23]). However, interconversions of the corresponding nitro complexes were achieved without intervention of base hydrolysis, and as interconversion of chloro and nitro complexes (with both imine and amine ligands) appeared to occur without any isomerization, it was assumed that the structures of chloro–imine complexes reflected those of the chloro–amine complexes derived from reduction. Nonetheless, there was an inconsistency in that while spectra of [Co(tetraenim)Cl]$^{2+}$ and [Co(Metetraenim)Cl]$^{2+}$ implied a major difference in structure, spectra of the reduction products indicated similar isomers were produced. Although some alternative structures could be excluded on the basis of the α-configuration of the parent [Co(trien)($\mathrm{H_2NCH_2COCH_3}$)Cl]$^{2+}$ ion, the possibility remained that they could be diastereomers (related by inversion at C and N) with the basic αα-[Co(tetraen)Cl]$^{2+}$ structure **6**. The difficulty was, therefore, resolved by X-ray crystal structure determinations (Figure 1). The results of the structure determinations (Tables II and III and Tables SUP-1–SUP-8 (supplementary material)) are consistent with the above stoichiometries and stereochemistry, with the reservation of the noted abnormal features in the needle phase (isomer N) and the location of a difference map artifact satisfactorily modeled as water for crystallization in the tablet phase (isomer T) (see Experimental Section). The cobalt environments of the two isomers are only trivially different (Tables II and III and Figure 1) with a discontinuity in the torsion angle signs to either side of the bond N(7)–C(8). The data used for all structural assignments based on visible spectra are summarized in Table I.

Empirical comparisons of $^1$H NMR spectra support the assignments based on visible spectra and add some subtle details. Aside from resonances assignable to the $\mathrm{NH_2R}$ ligands, the spectra of all "red" [Co(tren)($\mathrm{NH_2R}$)Cl]$^{2+}$ complexes, for example, are

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(32) Buckingham, D. A.; Cresswell, P. J.; Sargeson, A. M. *Inorg. Chem.* **1975**, *14*, 1485.

(33) (a) Buckingham, D. A.; Edwards, J. D.; McLaughlin, G. M. *Inorg. Chem.* **1982**, *21*, 2770. (b) Buckingham, D. A.; Clark, C. R.; Lewis, T. W. *Inorg. Chem.* **1979**, *18*, 2041.

(34) Jackson, W. G.; Sargeson, A. M. In *Rearrangements in Ground and Excited States*; de Mayo, P. Ed.; Academic: New York, 1980; Vol. 2, Essay II, p 273.

(35) Swaddle, T. W. *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 95.

(36) Buckingham, D. A.; Dwyer, M.; Sargeson, A. M.; Watson, K. J. *Acta Chem. Scand.* **1972**, *26*, 2813.

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

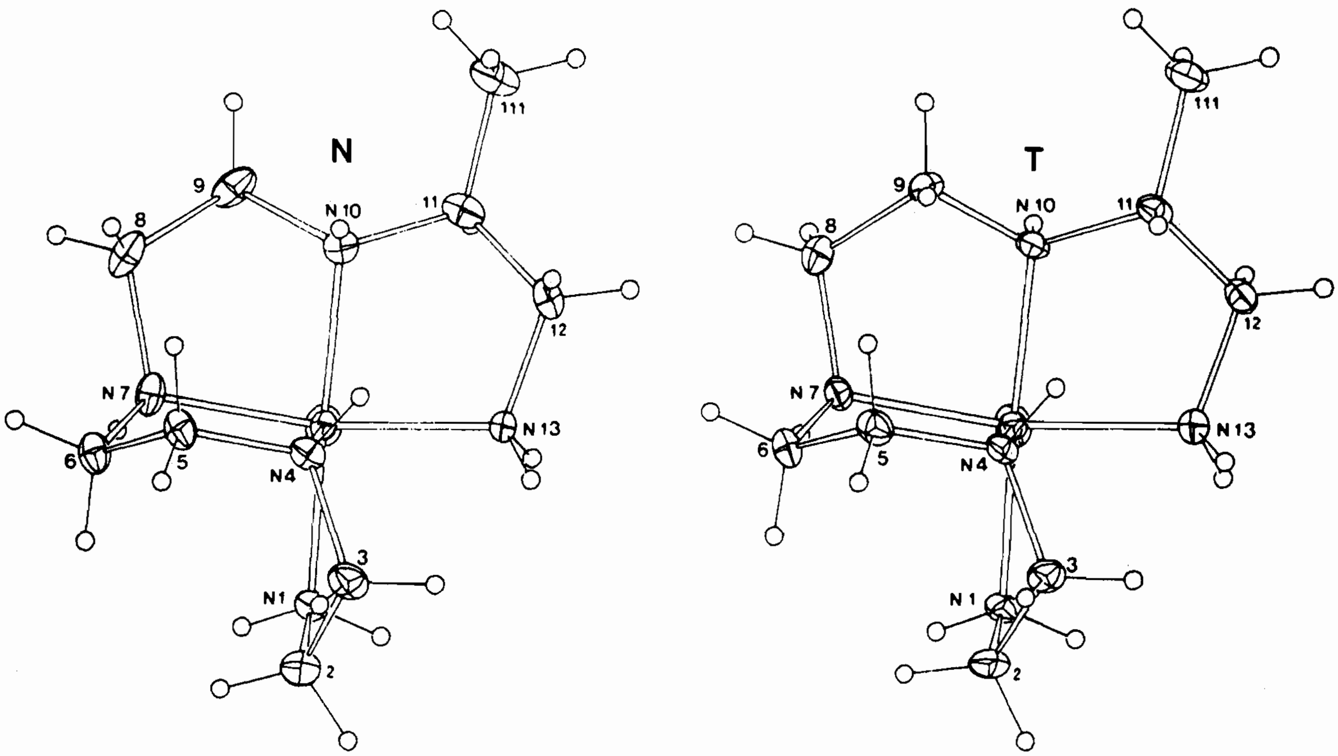

**Figure 1.** Crystal structures of the diastereoisomeric $(R)_N(S)_C$- (N isomer) and $(S)_N(R)_C$-$\alpha\alpha$-[Co(Metetraen)]$^{2+}$ (T isomer) ions showing projections of the two cations down the Co–C(1) bond. Thermal ellipsoids (20%) and atom numbering are given for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å. For the tabular form (T isomer), the chirality of the asymmetric unit has been reversed.

**Table II.** Non-Hydrogen Atom Coordinates for the N and T Isomers of $\alpha\alpha$-[Co(Metetraen)Cl]$^{2+}$

| | N isomer | | | T isomer | | |
|---|---|---|---|---|---|---|
| atom | *x* | *y* | *z* | *x* | *y* | *z* |
| Co | 0.37506 (3) | 0.46843 (7) | 0.37197 (9) | 0.29761 (8) | 0.7345 (1) | 0.1206 (1) |
| Cl(1) | 0.36948 (6) | 0.2831 (1) | 0.3371 (2) | 0.4555 (2) | 0.7373 (2) | −0.0603 (2) |
| N(1) | 0.3889 (2) | 0.4332 (5) | 0.5517 (5) | 0.2266 (5) | 0.6981 (6) | −0.0390 (7) |
| C(2) | 0.3951 (3) | 0.5285 (8) | 0.6366 (8) | 0.1103 (7) | 0.6732 (9) | 0.0241 (9) |
| C(3) | 0.4056 (3) | 0.6273 (7) | 0.5521 (7) | 0.0679 (6) | 0.7533 (8) | 0.1629 (9) |
| N(4) | 0.3771 (2) | 0.6212 (4) | 0.4339 (5) | 0.1537 (5) | 0.7157 (6) | 0.2603 (6) |
| C(5) | 0.3306 (3) | 0.6624 (6) | 0.4565 (7) | 0.1543 (6) | 0.5617 (8) | 0.3531 (9) |
| C(6) | 0.3001 (3) | 0.5651 (6) | 0.4896 (7) | 0.2412 (6) | 0.4524 (8) | 0.2689 (9) |
| N(7) | 0.3107 (2) | 0.4785 (5) | 0.3955 (6) | 0.3415 (5) | 0.5240 (6) | 0.2029 (6) |
| C(8) | 0.2880 (3) | 0.5015 (7) | 0.2654 (9) | 0.4114 (7) | 0.5164 (8) | 0.320 (1) |
| C(9) | 0.3176 (3) | 0.4685 (6) | 0.1577 (8) | 0.3775 (6) | 0.6563 (8) | 0.3977 (9) |
| N(10) | 0.3629 (2) | 0.5043 (4) | 0.1923 (6) | 0.3710 (5) | 0.7812 (6) | 0.2698 (7) |
| C(11) | 0.4008 (3) | 0.4649 (6) | 0.1107 (7) | 0.3243 (6) | 0.9336 (8) | 0.3091 (9) |
| C(111) | 0.3982 (4) | 0.5015 (8) | −0.0294 (8) | 0.3927 (7) | 0.9897 (9) | 0.400 (1) |
| C(12) | 0.4414 (2) | 0.5021 (6) | 0.1803 (7) | 0.3188 (6) | 1.0280 (8) | 0.1559 (9) |
| N(13) | 0.4382 (2) | 0.4653 (5) | 0.3164 (5) | 0.2623 (5) | 0.9545 (6) | 0.0684 (7) |
| Cl(2) | 0.20730 (7) | 0.2558 (2) | 0.1948 (2) | 0.2862 (2) | 0.3214 (2) | 0.7794 (2) |
| O(21) | 0.2406 (2) | 0.2506 (5) | 0.2909 (6) | 0.2095 (8) | 0.311 (1) | 0.9145 (9) |
| O(22) | 0.2247 (3) | 0.3082 (7) | 0.0835 (6) | 0.3733 (6) | 0.1975 (8) | 0.7823 (9) |
| O(23) | 0.1716 (3) | 0.3232 (9) | 0.2380 (8) | 0.2330 (8) | 0.306 (1) | 0.664 (1) |
| O(24) | 0.1928 (3) | 0.1498 (6) | 0.168 (1) | 0.3249 (7) | 0.4562 (8) | 0.736 (1) |
| Cl(3) | 0.00997 (7) | 0.2697 (2) | 0.1271 (2) | 0.0163 (2) | 0.2001 (2) | 0.3531 (2) |
| O(31) | 0.0412 (3) | 0.242 (1) | 0.207 (1) | 0.0756 (6) | 0.1912 (7) | 0.4713 (7) |
| O(32) | −0.0338 (2) | 0.2565 (5) | 0.1742 (6) | −0.0959 (4) | 0.1869 (7) | 0.4228 (7) |
| O(33) | 0.0136 (2) | 0.3812 (6) | 0.079 (1) | 0.0582 (5) | 0.0808 (7) | 0.2641 (8) |
| O(34) | 0.0146 (4) | 0.208 (1) | 0.012 (1) | 0.0220 (6) | 0.3374 (7) | 0.2551 (7) |
| C(O1)[a] | 0.1237 (4) | 0.031 (1) | 0.871 (1) | 0.1839 (5) | 0.9828 (6) | 0.7580 (7) |
| C(O2)[a] | 0.3697 (9) | 0.230 (2) | 0.340 (3) | | | |

[a] For the N isomer, C(O1) and C(O2) have populations of 0.47 (2), 0.40 (3), respectively.

almost exactly superimposable. (Assignments of $NH_2R$ ligand resonances were based on the free ligand spectra, general correlations, and comparisons with related, simpler complex ion systems.[5]) While prominent shoulders to the longer wavelength side of the manifold of $^1A_{1g} \rightarrow {}^1T_{1g}$ origin in [Co(trien)($RNH_2$)Cl]$^{2+}$ complexes are characteristic of both the $\beta$-*p*-$\Delta(R)$ and $\beta$-*p*-$\Delta(S)$ configurations, only in the $\Delta(R)$ species is the most rapidly exchanging proton resonance to high field of the remaining NH resonances. The same is true of [Co(trien)gly]$^{2+}$ isomers,[21] and for this reason [Co(trien){$NH_2CH_2CH(OH)_2$}Cl]$^{2+}$ is assigned the $\beta$-*p*-$\Delta(R)$ structure (**2**) rather than the $\beta$-*p*-$\Delta(S)$ structure (or the equivalent catoptric forms).

Assignments, listed in the Experimental Section, of NH resonances in particular are based on chemical shift and exchange rate data that have been broadly examined and subjected to detailed analysis in closely related systems. Thus, it is well es-

**Table III.** Cobalt Atom Environment for the N and T Isomers of $\alpha\alpha$-[Co(Metetraen)Cl]$^{2+\,a}$

| | | angles subtended at Co | | | | |
|---|---|---|---|---|---|---|
| atom | | N(1) | N(4) | N(7) | N(10) | N(13) |
| Cl(1) | 2.265 (3)<br>(2.257 (2)) | 87.3 (2)<br>(88.3 (2)) | 169.7 (2)<br>(172.0 (2)) | 90.4 (2)<br>(91.9 (2)) | 93.0 (2)<br>(89.6 (2)) | 90.4 (2)<br>(89.6 (2)) |
| N(1) | 1.952 (6)<br>(1.964 (7)) | | 83.4 (2)<br>(84.4 (3)) | 96.0 (3)<br>(96.9 (3)) | 178.6 (3)<br>(176.4 (3)) | 94.0 (2)<br>(93.0 (3)) |
| N(4) | 1.948 (6)<br>(1.969 (6)) | | | 86.1 (2)<br>(85.9 (2)) | 96.4 (2)<br>(97.9 (3)) | 94.8 (2)<br>(93.8 (2)) |
| N(7) | 1.953 (6)<br>(1.965 (5)) | | | | 85.4 (3)<br>(86.0 (3)) | 170.0 (3)<br>(170.0 (2)) |
| N(10) | 1.944 (6)<br>(1.944 (7)) | | | | | 84.6 (2)<br>(84.2 (3)) |
| N(13) | 1.982 (6)<br>(1.982 (6)) | | | | | |

[a] Entries for isomer T are given in parentheses below those for isomer N. *r* is the cobalt–ligand atom distance (Å), other entries are the angles (deg) subtended at the cobalt atom by the relevant atoms at the head of the associated row and column.

tablished[38,39] for Co(III) complexes that NH trans to Cl, for example, resonates upfield of NH trans to N and that proton exchange rates increase in the order $NH_3 < NH_2R < NHR_2$.[39] Also, proton exchange of $NH_n$ trans to Cl is typically at least ~$10^2$ faster than when it is trans to saturated N donors.[38]

Other minor structural features that are clearly established from $^1$H NMR spectroscopy include the degree of hydration of carbonyl reactants and the distinction of carbinolamine and imine species. These will be discussed in more detail.

More complex stereochemical problems require consideration in the [Co(trenphenol)Cl]$^{2+}$, [Co(trenphen)Cl]$^{2+}$, [Co(trenpn)-Cl]$^{2+}$, and [Co(Metetraen)Cl]$^{2+}$ systems in that diastereomerism may also be associated with the presence of asymmetric carbon centers. Although neither spectroscopic nor chromatographic experiments provided evidence of such isomerism and the condensation reaction forming the related [Co(trenenol)Cl]$^{2+}$ complex is known[5c] to be stereospecific, little evidence is available to assign isomeric preferences in these compounds. Strain energy minimization calculations were therefore made of the diastereomers of *s*-[Co(trenpn)Cl]$^{2+}$ (Figure 2). Details of the energy functions and the force field used have been described previously.[21d] Initial coordinates for the calculations were obtained by modification of structural coordinates for *s*-[Co(trenen)Cl]$^{2+}$, and positions for the methyl group were obtained by using the program CONTACTA.[40] The calculated structures of minimum energy are illustrated in Figure 2. Atomic coordinates are listed in Table IV, and a comparison of the energy sums is given in Table V. These calculations use the summation of nonbonded interactions over the entire molecule rather than over a limited range. The inclusion of these terms gives an improved comparison of strain energies and lower absolute energies with little or no effect on the structural parameters.

A comparison of the data (Table III) for the two structures indicates that the *SS* isomer is more strained than the *RS* isomer and that the larger part of this difference occurs in bond angle deformations. The energy difference is almost wholly due to non-bonded interactions of the methyl group hydrogen atoms with H(3), H(8) and H(23) in the *SS* isomer, whereas these steric effects are entirely relived in the *SR* isomer. The steric strain calculations have been shown to be valid in a relative sense for diastereoisomers where the calculations reproduced the geometry observed in the crystal[24,25] and for instances where isomers were equilibrated. Hence, it is assumed that the isolated *s*-[Co(trenpn)Cl]$^{2+}$ isomer is the (*R,S*) isomer plus its enantiomer and that *s*-[Co(trenphen)Cl]$^{2+}$ is likely to adopt the same structure. If the phenyl group in *s*-[Co(trenphenol)Cl]$^{2+}$ adopts the same orientation as in *s*-[Co(trenphen)Cl]$^{2+}$, the hydroxyl group is also well placed to hydrogen bond to an $NH_2$ group, and these two factors are the basis of the assignment of the configuration for

**Table IV.** Calculated Atomic Coordinates for the [Co(trenpn)Cl]$^{2+}$ Ions

| | *SS* isomer | | | *SR* isomer | | |
|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | *x* | *y* | *z* |
| Co | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| N(1) | 1.946 | 0.000 | 0.000 | 1.949 | 0.000 | 0.000 |
| N(2) | 0.128 | 1.927 | 0.000 | 0.094 | 1.940 | 0.000 |
| N(3) | −1.922 | 0.255 | 0.099 | −1.927 | 0.205 | 0.097 |
| N(4) | −0.127 | 0.017 | −1.953 | −0.124 | 0.003 | −0.952 |
| N(5) | −0.091 | −0.235 | 1.950 | −0.065 | −0.208 | 1.957 |
| Cl | −0.061 | −2.225 | −0.142 | −0.022 | −2.230 | −0.122 |
| C(1) | 2.444 | 1.381 | −0.307 | 2.432 | 1.413 | −0.117 |
| C(2) | 1.519 | 2.404 | 0.307 | 1.432 | 2.321 | 0.552 |
| C(3) | −0.994 | 2.433 | 0.840 | −1.074 | 2.424 | 0.792 |
| C(4) | −2.231 | 1.715 | 0.353 | −2.280 | 1.660 | 0.308 |
| C(5) | −2.452 | −0.202 | −1.228 | −2.441 | −0.298 | −1.220 |
| C(6) | −1.547 | 0.321 | −2.314 | −1.556 | 0.241 | −2.317 |
| C(7) | −2.407 | −0.606 | 1.225 | −2.381 | −0.636 | 1.252 |
| C(8) | −1.512 | −0.374 | 2.411 | −1.484 | −0.345 | 2.427 |
| C(9) | 1.849 | 2.630 | 1.765 | 1.753 | 3.768 | 0.260 |
| H(1) | 2.307 | −0.308 | 0.914 | 2.309 | −0.420 | 0.869 |
| H(2) | 2.284 | −0.654 | −0.721 | 2.296 | −0.563 | −0.798 |
| H(3) | 3.456 | 1.504 | 0.085 | 3.406 | 1.514 | 0.366 |
| H(4) | 2.480 | 1.526 | −1.388 | 2.533 | 1.679 | −1.171 |
| H(5) | 1.672 | 3.354 | −0.211 | 1.469 | 2.169 | 1.631 |
| H(7) | −0.073 | 2.246 | −0.958 | 0.007 | 2.310 | −0.958 |
| H(8) | −0.835 | 2.240 | 1.897 | −0.919 | 2.283 | 1.859 |
| H(9) | −1.109 | 3.508 | 0.695 | −1.226 | 3.490 | 0.609 |
| H(10) | −3.018 | 1.819 | 1.101 | −3.081 | 1.761 | 1.042 |
| H(11) | −2.585 | 2.203 | −0.555 | −2.656 | 2.116 | −0.616 |
| H(13) | −2.476 | −1.291 | −1.280 | −2.426 | −1.388 | −1.252 |
| H(14) | −3.467 | 0.170 | −1.377 | −3.470 | 0.032 | −1.375 |
| H(15) | −1.798 | −0.166 | −3.259 | −1.788 | −0.272 | −3.253 |
| H(16) | −1.684 | 1.396 | −2.440 | −1.733 | 1.307 | −2.462 |
| H(17) | 0.139 | −0.894 | −2.354 | 0.184 | −0.897 | −2.349 |
| H(18) | 0.496 | 0.722 | −2.371 | 0.471 | 0.735 | −2.366 |
| H(19) | −3.437 | −0.351 | 1.481 | 3.416 | −0.403 | 1.509 |
| H(20) | −2.387 | −1.661 | 0.953 | −2.334 | −1.698 | 1.011 |
| H(21) | −1.832 | 0.520 | 2.948 | −1.814 | 0.564 | 2.931 |
| H(22) | −1.595 | −1.222 | 3.094 | −1.555 | −1.166 | 3.143 |
| H(23) | 0.337 | 0.538 | 2.468 | 0.384 | 0.570 | 2.456 |
| H(24) | 0.429 | −1.086 | 2.205 | 0.453 | −1.061 | 2.216 |
| H(25) | 1.932 | 1.692 | 2.305 | 1.016 | 4.415 | 0.736 |
| H(26) | 2.808 | 3.144 | 1.838 | 2.741 | 4.015 | 0.652 |
| H(27) | 1.098 | 3.262 | 2.236 | 1.743 | 3.952 | −0.815 |

**Table V.** Minimized Strain Energy Terms (kJ mol$^{-1}$) for the Two Isomers of [Co(trenpn)Cl]$^{2+}$

| term | *SS* isomer | *SR* isomer | $U_{SS} - U_{SR}$ |
|---|---|---|---|
| bond deformation | 4.98 | 3.18 | 1.80 |
| valence angle deformation | 37.3 | 18.5 | 18.8 |
| nonbonded interactions | 3.77 | 3.02 | $0.75^2$ |
| torsional interactions | 30.1 | 24.7 | 5.4 |
| total strain energy | 76.2 | 49.4 | 26.8 |

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(38) Bramley, R. D.; Creaser, I. I.; Mackey, D. J.; Sargeson, A. M. *Inorg. Chem.* **1978**, *17*, 244.

(39) Tobe, M. L. *Adv. Inorg. Bioinorg. Mech.* **1982**, *2*, 1 and references therein.

(40) Maxwell, I. E.; Healy, M. J. "CONTACTA—A Program to Calculate Bonded Hydrogen Atom Positions"; University of Sydney and Australian National University, 1969.

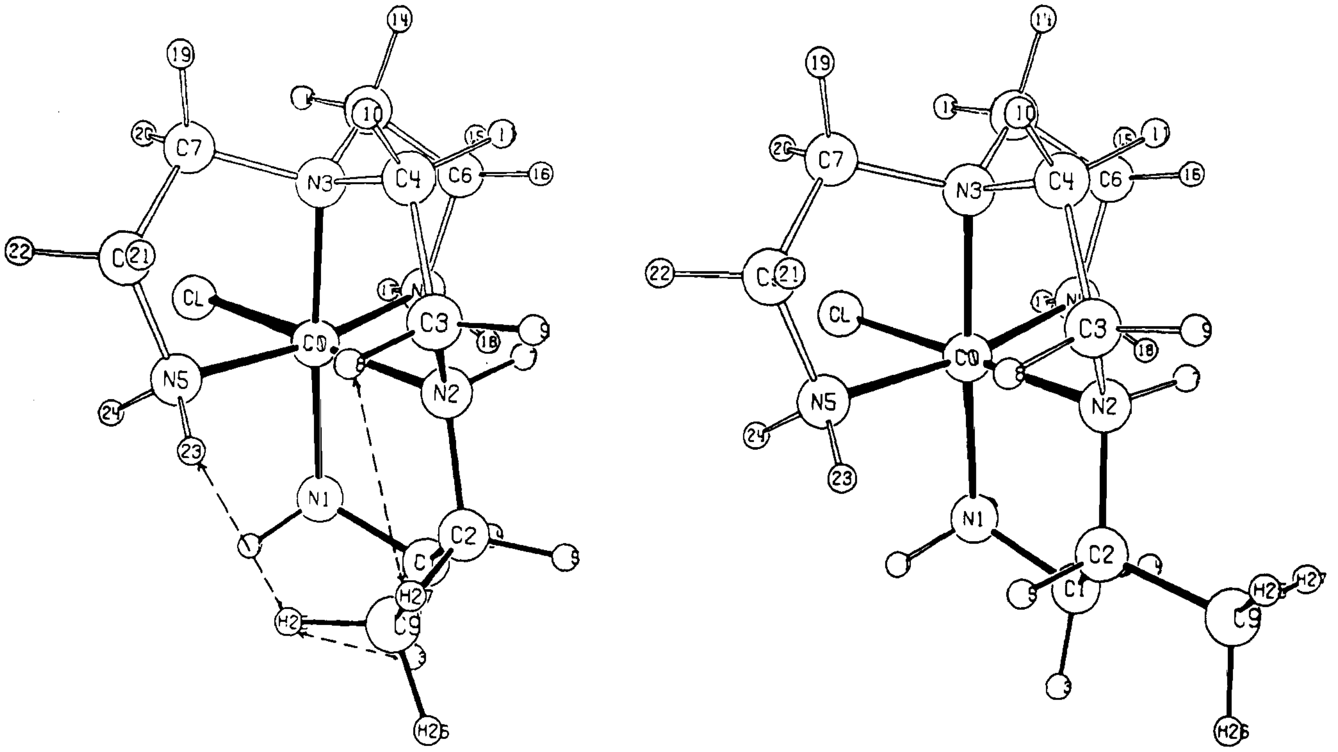
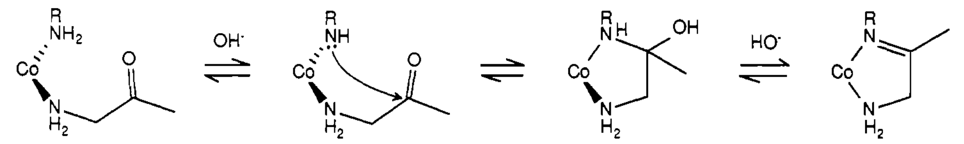


**Figure 2.** Strain energy minimized structures of the two $[Co(trenpn)Cl]^{2+}$ diastereoisomers. Intramolecular close contacts are only shown where these differ significantly between the two structures.

**Scheme I**



the $[Co(trenphenol)Cl]^{2+}$ ion isolated.

**Synthesis and Reaction Pathways. Aminocarbonyl Ligand Complexes.** The high reactivity of aminocarbonyl compounds renders them attractive in synthesis but creates some problems in the preparation of their metal complexes. We have employed two procedures to surmount these difficulties, the more obvious being the protection of the carbonyl group during attachment of the amine function to Co(III). Acetals or ketals of aminocarbonyl compounds are readily handled materials with good ligating properties, though they are not necessarily readily accessible compounds themselves. Amino alcohols, in contrast, are commonly available, and hence there is considerable attraction in the notion of oxidation of the hydroxyl functionality to a carbonyl group after attachment of the amine group to (and protection of it by) the metal ion. We have previously exploited such a procedure in the synthesis of $(NH_3)_5CoNH_2CH_2COCH_3{}^{3+}$[5c] and have presently utilized it in the conversion of coordinated $NH_2CH_2CH(OH)C_6H_5$ to coordinated $NH_2CH_2COC_6H_5$. However, amino alcohols frequently act as chelates, such complexes are more difficult to oxidize and, more importantly, oxidation of Co(III) complexes with reagents such as $Cr_2O_7{}^{2-}/H_3O^+$ usually proceeds in relatively poor yield due to the production of some Co(II) species through reactions of intermediate radicals.[41] Thus, it remains useful to have the protected carbonyl group ligand procedure as an alternative synthesis.

The reactions of $[Co(tren)Cl_2]^+$ with protected aminocarbonyl compounds and amino alcohols appear less complicated than those of $[Co(trien)Cl_2]^+$ in that only red complexes with the "*p*"[32,33] structure (**1**) of $[Co(tren)(NH_2R)Cl]^{2+}$ were obtained. The surprising subtlety of factors that may operate in reactions of this kind is revealed in the fact that while the known reaction[5c] between aminoacetaldehyde *dimethyl* acetal and $\alpha$-$[Co(trien)Cl_2]^+$ (or the $\beta$ isomer) generates exclusively $\alpha$-$[Co(trien)\{H_2NCH_2CH(OCH_3)_2\}Cl]^{2+}$, the presently reported reaction between aminoacetaldehyde *diethyl* acetal and $\beta$- or $\alpha$-$[Co(trien)Cl_2]^+$ generates largely $\beta$-*p*-$[Co(trien)\{H_2NCH_2CH(OC_2H_5)_2\}Cl]^{2+}$. An explanation for this behavior is not obvious.

Deprotection of the protected aminocarbonyl complexes was readily achieved by acid-catalyzed hydrolysis.[42] As expected from earlier work, coordinated aminoacetaldehyde was present in the completely hydrated form in the solid and in aqueous solution. Thus, no carbonyl group stretching absorption could be detected in the IR spectrum of $\beta$-*p*-$\Delta$(*R*)-$[Co(trien)\{H_2NCH_2CH(OH)_2\}Cl]Cl_{1.5}Br_{0.5}$ and no formyl proton resonance was observed in the $^1H$ NMR spectrum, while a triplet at $\delta$ 5.27, 5.33, and 5.38, assignable to the gem diol $CH_2CH(OH)_2$ group methine proton, integrated as one proton. Not surprisingly, the aminoacetone complexes *p*-$[Co(tren)(H_2NCH_2COCH_3)Cl]^{2+}$ and $\alpha$-$[Co(trien)(H_2NCH_2COCH_3)Cl]^{2+}$ both showed only a sharp methyl signal at $\delta$ 2.26, with no evidence of a higher field signal attributable to hydrate. While the complexity of the $^1H$ NMR spectrum of *p*-$[Co(tren)(H_2NCH_2COC_6H_5)Cl]^{2+}$ does not allow conclusions as to its degree of hydration to be readily drawn, a strong $\nu_{C=O}$ band at 1709 $cm^{-1}$ was detected in the IR spectrum of its perchlorate salt, and kinetic evidence (see ahead) implies that the carbonyl group is not extensively hydrated in solution. These conclusions are consistent with those for related 2-oxocarboxylato complexes.[8,43,44]

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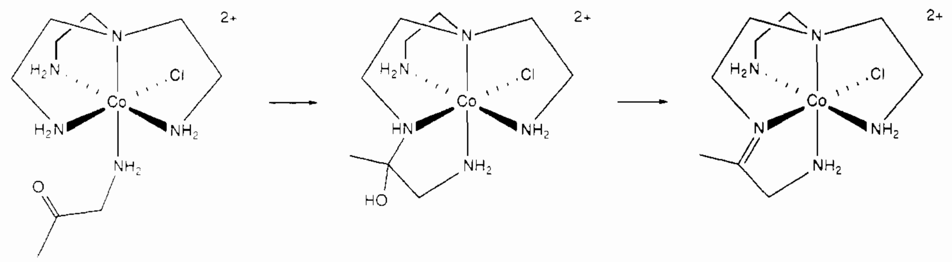
(41) Gainsford, A. R.; Watson, A. D., unpublished observations.

(42) Approximate NMR measurements indicated similar half-lives ~ 1 h (in 1 mol $L^{-1}$ DCl, ~298 K) for all complexes presently investigated.

(43) Price, H. J.; Taube, H. *J. Am. Chem. Soc.* **1967**, *89*, 269; *Inorg. Chem.* **1968**, *7*, 1.

(44) Occupati, G.; Pratt, L. *J. Chem. Soc., Dalton Trans.* **1973**, 1699.

**Scheme II**



**Cyclization Reactions of *p*-$[Co(tren)(H_2NCH_2COR)Cl]^{2+}$ Complexes.** When *p*-$[Co(tren)(H_2NCH_2COCH_3)Cl]^{2+}$ was dissolved in $D_2O$ buffer solutions of pH <6.6, the $^1H$ NMR spectrum showed a sharp singlet at $\delta$ 2.25 ($COCH_3$) which rapidly disappeared while a new singlet at $\delta$ 1.62 arose. This resonance in turn diminished in intensity at a rate approximately one-third of the rate of its appearance, to be replaced by a third singlet at $\delta$ 2.30. These changes are consistent with an intramolecular reaction involving the intermediate formation of carbinolamine, which ultimately decays to an imine, Scheme I. The fact that the carbinolamine was directly detected by NMR spectroscopy simplified subsequent analysis of the cyclization kinetics by allowing the observed rate constants to be assigned to particular steps.[45]

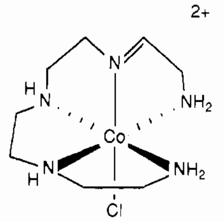
Changes in the visible absorption spectrum of *p*-$[Co(tren)(H_2NCH_2COCH_3)Cl]^{2+}$ were completely consistent with both the NMR observations and the properties of isolated carbinolamine species such as *s*-$[Co(trenenol)Cl]^{2+}$ [5c] and *s*-$[Co(trenphenol)Cl]^{2+}$. Thus, the lowest energy absorption maximum shifted from its initial position at 513 nm to the slightly shorter wavelength of 512 nm (with a slight increase in absorbance) and then, more slowly, to 496 nm, the value observed for the isolated *s*-$[Co(trenpnim)Cl]^{2+}$ complex. At later times, sharp isosbestic points at 526, 419, 372, and 323 nm were observed while large absorbance changes occurred between 510 and 480 nm. Spectrophotometric rate measurements (see ahead) were therefore made at 526 nm to determine the rate constants for carbinolamine formation and at 496 nm for its decay to imine.

Ion-exchange chromatography of reaction mixtures after $10t_{1/2}$ for the second reaction step revealed only one product, spectroscopically identical with the isolated *s*-$[Co(trenpnim)Cl]^{2+}$ complex. In media of pH >6.6, however, a second product was apparent, though this was converted to *s*-$[Co(trenpnim)Cl]^{2+}$ on heating in HCl and was easily generated by reacting the isolated chloro–imine complex with NaOH. Its origin simply seemed to be the result of a subsequent base hydrolysis reaction at higher pH values. Thus, the cyclization reaction at pH values of <6.6 can be simply represented as in Scheme II.

This process, of course, requires that exchange of $NH_2$ protons trans to Cl must occur at a rate at least equal to that of carbinolamine formation and that these protons are lost in the product. Exchange of other $NH_2$ protons is unnecessary, though it need not be slower than the cyclization reaction. In fact, the initial $^1H$ NMR spectrum of *p*-$[Co(tren)(H_2NCH_2COCH_3)Cl]^{2+}$ shows three broad NH resonances at $\delta$ 4.70, 4.95, and 5.20, corresponding to two, four, and two protons respectively. In $D_2O$/acetate buffers the signal at $\delta$ 4.70 decays approximately 10 times faster (see ahead) than cyclization occurs, while the $\delta$ 4.95 and 5.20 signals do not appreciably diminish and instead are retained as resonances at $\delta$ 5.0 and 5.5 in the imine product. Thus, it appears that potentially reversible condensations at the $NH_2$ centers cis to Cl cannot play a significant role in the observed reaction and that the $\delta$ 4.70 resonance must be identified as that due to the $NH_2$ protons trans to Cl in the reactant. The relatively high-field signal for these protons is consistent with data for simpler systems.[38]

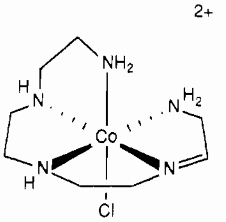
In media of pH <5.5, reactions of *p*-$[Co(tren)(H_2NCH_2COC_6H_5)Cl]^{2+}$ closely paralleled those of the aminoacetone analogue, with analysis of the system being simplified by the ability to isolate the carbinolamine intermediate. The visible absorption spectrum of *p*-$[Co(tren)(H_2NCH_2COC_6H_5)Cl]^{2+}$ ($\lambda_{max}$ 511 nm) changed relatively rapidly, with absorbance increases near 355 and 505 nm, to one showing a maximum at 504 nm, as observed for the isolated carbinolamine, and then changed to one with a maximum at 497 nm, accompanied by a large increase in absorbance near 496 nm. Only a single product, spectroscopically identical with the isolated *i*-$[Co(trenphenim)Cl]^{2+}$, could be detected by ion-exchange chromatography of reaction mixtures. Though detailed proton-exchange measurements were not made on *p*-$[Co(tren)(H_2NCH_2COC_6H_5)Cl]^{2+}$, its reaction pathway seems to be identical with that given above for the aminoacetone complex.

**Cyclization Reactions of $[Co(trien)(H_2NCH_2COR)Cl]^{2+}$ Complexes.** Despite the apparently complete hydration of the carbonyl group in *β*-*p*-Δ(*R*)-$[Co(trien)\{H_2NCH_2CH(OH)_2\}Cl]^{2+}$, its condensation with adjacent amino groups is extremely rapid in neutral aqueous media, as observed with related systems.[5c,6] Unfortunately, the cyclization is accompanied by extensive (<80%) loss of chloride, giving complicated kinetics that were not analyzed, though it was anticipated from the behavior of *p*-$[Co(tren)\{H_2NCH_2CH(OH)_2\}Cl]^{2+}$ [6] that a carbinolamine intermediate would be involved. The complex is unusual in the present series in that three inequivalent cyclization sites are available. However, rationalization[5c] of the stereospecific cyclization of *α*-$[Co(trien)\{H_2NCH_2CH(OH)_2\}Cl]^{2+}$ as reflecting reaction through the most acidic NH group led to the expectation that exclusive formation of the "angular" imine complex *αβ*-*i*-$[Co(tetraenim)Cl]^{2+}$ (**7**) should occur rather than formation of the "planar" imine complex *β*-*trans*-*p*-$[Co(tetraenim)Cl]^{2+}$ (**8**). In fact, the exclusive product is the "angular" imine and it appears that initial addition to the carbonyl center of the amido ion trans to Cl must be much faster than that of the amido ion cis to Cl. Also, this step and further steps must be irreversible. Lesser bond distortion factors in a planar imine product are not of consequence in deciding the regiospecificity of the cyclization.



αβ-i-[Co(tetraen-im)Cl]$^{2+}$

**7**



β*trans*- p-[Co(tetraen-im)Cl]$^{2+}$

**8**

When the $^1H$ NMR spectrum of *α*-$[Co(trien)(H_2NCH_2COCH_3)Cl]^{2+}$ in neutral media was monitored over time, the initial $\delta$ 2.26 $CH_3$ resonance was observed to decay and to be replaced by one at $\delta$ 2.42 without an intermediate high-field signal being detectable. Thus, it appears that a carbinolamine never becomes an appreciable system component and that the condensation can be treated as a single step. A further observed difference from the related tren system was that all amine protons exchange at a rate at least 5 times faster than the condensation occurred. As well, chloride ligand loss was competitive with condensation to the extent that, on completion of condensation, only ~20% of the chloro–imine species was present.

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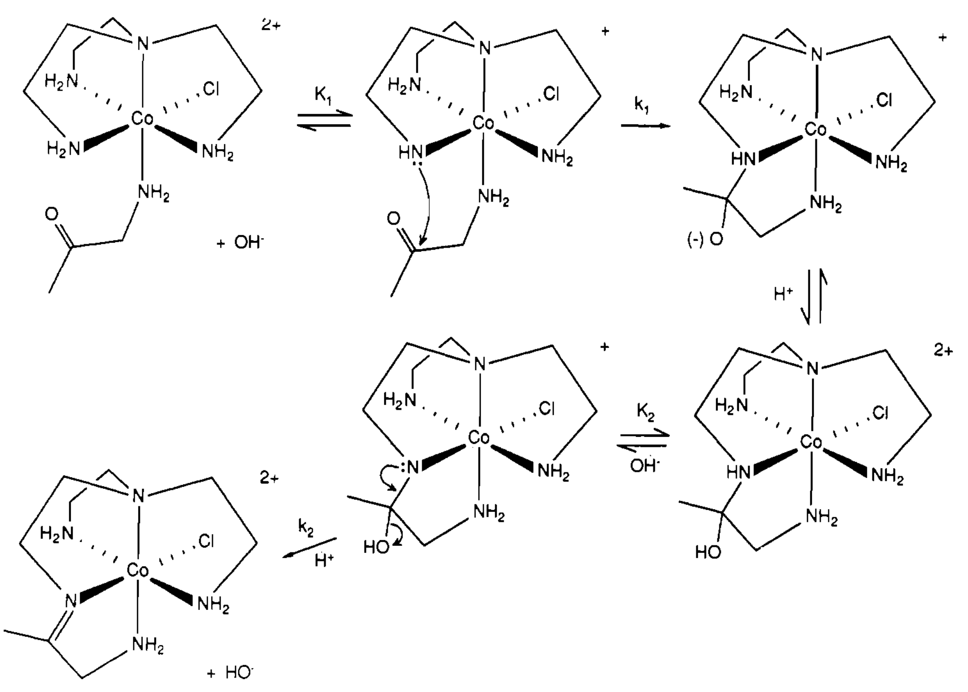
(45) Harrowfield, J. MacB.; Jackson, W. G.; Vowles, P. D. *Int. J. Chem. Kinet.* **1977**, *9*, 535.

(46) Fisher, R.; Bye, J. *Bull. Soc. Chim. Fr.* **1974**, 2920.

Scheme III



Perhaps the most surprising feature of the condensation reaction is, however, that a carbinolamine analogous to that obtained from $\alpha$-[Co(trien){$H_2NCH_2CH(OH)_2$}Cl]$^{2+}$ is not the reaction product. The formation of what is taken (see above) to be the "planar" imine product $\alpha\beta$-*i*-[Co(Metetraenim)Cl]$^{2+}$ implies that the reaction is not under reactant acidity control. This may be because the approach of the carbonyl group at the deprotonated –NH group trans to Cl is sterically hindered. The methyl group would interact strongly with trien methylene groups or a primary amine center. The $^1H$ NMR spectrum of $\alpha$-[Co(trien)($H_2NCH_2COCH_3$)Cl]$^{2+}$ shows four broad amino proton resonances at $\delta$ 4.40, 5.24, 6.18, and 6.56, corresponding to two, four, one, and one protons, respectively. By comparison with the spectrum of $\alpha$-[Co(trien)($NH_3$)Cl]$^{2+}$ the $\delta$ 4.40 resonance is assigned to the $NH_2$ group of aminoacetone, while the $\delta$ 6.18 and 6.56 resonances must obviously be due to secondary NH groups of trien; the $\delta$ 5.25 resonance must represent both (inequivalent) primary amino group protons. These appear to exchange at one rate, implying that if there is no acidity difference between centers that can give rise to "planar" or "angular" imine products, the reaction may be controlled by the stereochemistry of the activated complex for the addition of the nucleophile.

**Hydrolysis Reactions of Chloro–Imine Complexes and Their Reduction Products.** In neutral or acidic aqueous media, all the new chloro–imine complexes and their saturated derivatives show spectral changes consistent with the slow replacement of $Cl^-$ by water at the Co(III) ion. In basic solutions, very much faster changes consistent with the formation of hydroxo species occur. In most cases, however, the reactions appeared (unless prolonged in base) to give single products that, when heated in HCl, regenerated only the reactant complexes. Hence, the reactions have all been treated as simple substitution processes not involving stereochemical changes. However, this is not the case for the [Co(tetraen)Cl]$^{2+}$ complexes, which have been studied previously.[23]

**Cyclization Kinetics.** The cyclization of *p*-[Co(tren)($H_2NCH_2COCH_3$)Cl]$^{2+}$ to *i*-[Co(trenpnim)Cl]$^{2+}$ was analyzed as consecutive first-order irreversible reactions (two steps). By appropriate choice of monitoring wavelength, the rate constants were obtained for the sequence

$$[\mathrm{Co(tren)(H_2NCH_2COCH_3)Cl}]^{2+} \xrightarrow{k_1} [\mathrm{Co(trenpnol)Cl}]^{2+} \xrightarrow{k_2} [\mathrm{Co(trenpnim)Cl}]^{2+}$$

as simple linear, ln $|A_t - A_\infty|$ versus time plots.[45] Linearity was observed for at least $4t_{1/2}$ in all instances. Rates were measured at an ionic strength of 1.0, maintained with $NaClO_4$, over a range of temperatures and pH, with pH control being attained by pH-stat titration and the use of buffers. Rates were observed to be independent of buffer concentration and the nature of the buffer. The results are summarized in Table SUP-9 (supplementary material). It is apparent that over the relatively narrow pH range studied, both rate constants show a first-order dependence on [$OH^-$]. The simplest reaction mechanism consistent with this and the reaction stereochemistry is shown in Scheme III.

The rate expression deduced for this mechanism, by applying the steady-state approximation to all deprotonated species and by assuming reprotonation rates[47] considerably exceeding the rates of the irreversible steps, requires that the following equations are obeyed.

$$k_{1(\mathrm{obs})} = k_1K_1[\mathrm{OH^-}] = 4.1\ (1) \times 10^6[\mathrm{OH^-}]\ \mathrm{s^{-1}}$$

$$k_{2(\mathrm{obs})} = k_2K_2 = 1.5\ (1) \times 10^6[\mathrm{OH^-}]\ \mathrm{s^{-1}}$$

Here, $K_1$ and $K_2$ are the equilibrium constants for the $OH^-$ ion reaction with amino protons of the reactant carbonyl and intermediate carbinolamine complexes, respectively. Few direct measurements of such equilibrium constants are available,[12,47,48] and the general observation of the lack of saturation kinetics in the base hydrolysis of cobalt(III) acidoamine complexes is usually taken to signify that typical values would be $\ll 1$. For the secondary amine protons on [Co($NO_2$)$_2$sar)]$^{3+}$, $K_b \sim 10^6$[12] ($K_b = K_a/K_w$) and an estimate of $K_b \sim 0.1$ has been made for Co(en)$_3^{3+}$.[49] Given the acidity enhancing effect of a trans Cl group, it is likely that $K_1$ and $K_2$ have values close to 1. Thus, the magnitudes of $k_1$ and $k_2$ should be similar, with an approximate value at 298 K of $10^6$ $s^{-1}$. This value is sufficiently small to be consistent with the approximations mentioned above since the base reprotonation rates should be close to the diffusion-controlled limit.[34,47]

As the temperature dependence of $K_1$ and $K_2$ is unknown, enthalpic and entropic influences on the reaction steps could not be factorized into preequilibrium and rate contributions. From the temperature dependence of $k_{1(\mathrm{obs})}$ and $k_{2(\mathrm{obs})}$, however, apparent

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(47) Pitner, T. P.; Martin, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 4400.

(48) See ref 33b for a summary of relevant literature. See also: Martell, A. E.; Raleigh, C. J. *Inorg. Chem.* **1985**, *24*, 142.

(49) Goodall, D. M.; Hardy, M. J. *J. Chem. Soc., Chem. Commun.* **1975**, 919.

**Table VI.** Rate Data for Chloride Ion Substitution in *s*-$[Co(trenpnim)Cl]^{2+}$, *s*-$[Co(trenpn)Cl]^{2+}$, and *s*-$[Co(trenphen)Cl]^{2+}$ in Aqueous Media

| complex | temp, K | pH | $k_{obs}$, $s^{-1}$ | $k_{OH^-}$, $M^{-1}\ s^{-1}$ |
|---|---|---|---|---|
| $[Co(trenpn)Cl]^{2+}$ [a] | 323.2 | 1[e] | $1.69 \times 10^{-6}$ | |
| | 323.2 | 3[f] | $1.65 \times 10^{-6}$ | |
| $[Co(trenpn)Cl]^{2+}$ [b] | 298.2 | 8.36[g] | $2.04 \times 10^{-3}$ | 520 |
| | | 8.96[g] | $7.93 \times 10^{-3}$ | 510 |
| | | 9.10[g] | $10.8 \times 10^{-3}$ | 500 |
| | | 9.39[g] | $21.4 \times 10^{-3}$ | 510 |
| | | 9.78[g] | $50.9 \times 10^{-3}$ | 500 |
| $[Co(trenpnim)Cl]^{2+}$ [c] | 298.2 | 8.96[g] | $3.58 \times 10^{-3}$ | 23 |
| | | 9.10[g] | $4.75 \times 10^{-4}$ | 22 |
| | | 9.39[g] | $9.59 \times 10^{-4}$ | 23 |
| | | 9.78[g] | $22.7 \times 10^{-4}$ | 22 |
| $[Co(trenphen)Cl]^{2+}$ [d] | | 7.05[h] | $1.20 \times 10^{-3}$ | 6100 |
| | | 7.60[h] | $4.10 \times 10^{-3}$ | 6100 |
| | | 8.00[h] | $10.3 \times 10^{-3}$ | 6100 |

[a] $I = 1.0$ ($NaClO_4$). Absorbance measurements at 530 nm. $[Co] = 2 \times 10^{-3}$ mol $L^{-1}$. [b] $I = 1.0$ ($NaClO_4$). Absorbance measurements at 485 nm. $[Co] = 2 \times 10^{-3}$ mol $L^{-1}$. [c] $I = 1.0$ ($NaClO_4$). Absorbance measurements at 358 nm. [d] $I = 1.0$ ($NaCF_3SO_3$). Absorbance measurements at 490 nm. $[Co] = 2 \times 10^{-3}$ mol $L^{-1}$. [e] 0.100 mol $L^{-1}$ $HClO_4$. [f] 0.001 mol $L^{-1}$ $HClO_4$. [g] Diethanolamine buffers, $[B] + [BH^+] = 0.075$ mol $L^{-1}$. [h] Imidazole buffers, $[Im] + [ImH^+] = 0.075$ mol $L^{-1}$. [i] $k_{OH} = k_{obs}/[OH^-]$; $[OH^-]$ estimated by using pH + pOH = 13.77.[46]

overall activation parameters of $\Delta H^{*} = 42 \pm 4$ kJ $mol^{-1}$ and $\Delta S^{*} = +27 \pm 3$ J $K^{-1}$ $mol^{-1}$ for formation of the carbinolamine intermediate and of $\Delta H^{*} = 29 \pm 1$ kJ/$mol^{-1}$ and $\Delta S^{*} = -28 \pm 1$ J $K^{-1}$ $mol^{-1}$ for its dehydration to the imine can be calculated.

As noted previously, the cyclization of *p*-$[Co(tren)(H_2NCH_2COCH_3)Cl]^{2+}$ can be conducted under conditions where only exchange of the tren $NH_2$ protons trans to Cl is observed. This exchange was monitored in $CD_3COOD/CD_3CO_2Na/D_2O$ buffers ($I = 1.0$ at 298 ± 1 K) having pD values of 4.32 and 3.71.[50] Plots of log (peak area) versus time were linear, indicating half-lives of 250 s (pD 4.32) and 1050 s (pD 3.71). Assuming a rate law $k_{obs} = k_{ex}[OD^-]$, a mean $k_{ex}$ value of $(4.2 \pm 0.1) \times 10^7$ $M^{-1}$ $s^{-1}$ may be estimated. Comparison with the carbinolamine formation rate constant, $k_{1(obs)}$, at 298 K, $4.1 \times 10^6$ $M^{-1}$ $s^{-1}$, suggests that the carbonyl function must be captured, approximately, once in every ten proton exchanges. Similar high efficiencies of capture of deprotonated coordinated amines have been observed in the condensation of *cis*-$[Co(en)_2(H_2NCH_2CN)Cl]^{2+}$ to give an amidine chelate (one capture in 40 exchanges),[14] in cyclization of $\alpha$-$[Co(trien)\{H_2NCH_2CH(OH)_2\}Cl]^{2+}$ to a chelate carbinolamine (one capture in 30 exchanges),[5c] and in the cyclization of *cis*-$[Co(en)_2(H_2NCH_2COCH_3)_2]^{3+}$ to a carbinolamine (also one capture in 30 exchanges).[5a] Since inversion at chiral, deprotonated, coordinated N centers usually occurs some $10^4$–$10^6$ times more slowly than proton exchange,[34] it appears that particular diastereomeric configurations should be retained in intramolecular cyclization reactions of the type described herein.

The kinetics of the cyclization of *p*-$[Co(tren)(H_2NCH_2COC_6H_5)Cl]^{2+}$ were monitored ($\mu = 1.0$ NaCl) and analyzed in the same manner as for the aminoacetone complex ($k_1K_1 = 1.63\ (3) \times 10^7$ $M^{-1}$ $s^{-1}$ and $k_2K_2 = 4.8\ (1) \times 10^5$ $M^{-1}$ $s^{-1}$ at 25 °C, $\mu = 1.0$), though some additional measurements of the second reaction step were made by using the isolated carbinolamine intermediate. Results are summarized in Table SUP-10 (supplementary material). They are not remarkably different from those for the aminoacetone analogue and can be assessed similarly. The rapidity of the carbinolamine formation and strict first-order kinetics observed are taken as empirical evidence that the carbonyl group in *p*-$[Co(tren)(H_2NCH_2COC_6H_5)Cl]^{2+}$ is, like that for *p*-$[Co(tren)(H_2NCH_2COCH_3)Cl]^{2+}$, not hydrated.

Because of the complexity of the reactions, precise quantitative estimates of cyclization rates could not be made for the other complexes of aminoacetaldehyde and aminoacetone. However, approximate proton exchange measurements on $\alpha$-$[Co(trien)(H_2NCH_2COCH_3)Cl]^{2+}$ show that primary amino group proton exchange is ~60-fold slower than that of the proton of the secondary amino group, trans to Cl, so that if this exchange is at a rate similar to the analogous proton in $\alpha$-$[Co(trien)(NH_3)Cl]^{2+}$ ($k = 3 \times 10^7$ $M^{-1}$ $s^{-1}$),[20] the second order rate constant for primary amino group proton exchange should be $\sim 5 \times 10^5$ $M^{-1}$ $s^{-1}$. For a capture efficiency of 20%, this estimate leads to a condensation rate constant of $\sim 10^5$ $M^{-1}$ $s^{-1}$, a value that is compatible with overall observations.

**Kinetics of Chloride Ligand Substitution in Chloro–Imine and Chloro–Amine Complexes.** Limited aquation and base hydrolysis rate measurements were made for the stereochemically simpler trenpnim, trenpn, and trenphen complex ion systems. All reactions were observed to be single, first-order processes with rates dependent on pH but independent of buffer concentration, though $[Co(trenpnim)OH]^{2+}$ did undergo decomposition on prolonged standing in diethanolamine buffers. Rate data from absorbance/time measurements are summarized in Table VI.

The variations in base hydrolysis rate constants seen here as a consequence of functionalization of the [Co(trenen)Cl] skeleton are, unsurprisingly, similar to those observed in $[Co(tren)(NH_3)Cl]^{2+}$ [32,33] and $[Co(Metren)(NH_3)Cl]^{2+}$ [33] systems. That the imine complex is least reactive is consistent with the fact that introduction of the imine group corresponds to loss of the acidic NH proton in the *s*-$[Co(trenen)Cl]^{2+}$ [37] though the imine donor group will undoubtedly have a particular influence of its own on the reactivity of a conjugate base that must be derived from an amino group now cis to Cl. The relatively high reactivity of the $[Co(trenphen)Cl]^{2+}$ complex may reflect steric interactions of the large phenyl substituent that are relieved on the way to a five-coordinate intermediate.

## Conclusions

All the cyclization reactions presently described proceed rapidly and regiospecifically under mild conditions and are obviously a useful procedure for the systematic elaboration of multidentate ligand structures. The dominant factor in determining the cyclization regiospecificity appears to be the rate of proton exchange (assumed to parallel acidity[34,37]) at coordinated amino groups, and since this is sensitive to the nature of the trans-coordinated group, there is obviously the chance to direct cyclizations through variation in this ligand (i.e. Cl in the present instances).

The formation of amine complexes by reduction of coordinated imines with $BH_4^-$, as well as the cyclization reactions to form carbinolamine species, also appears to be stereospecific in all the present instances. This is possibly a reflection of the preference of carbon substituents for an equatorial disposition in 5-membered chelate rings[24,25,51] as indicated by the strain energy minimization calculations for the *s*-$[Co(trenpn)Cl]^{2+}$ diastereomers.

Quite apart from their stereospecificity, intramolecular reactions of the type described here and elsewhere are efficient ways of building up elaborate molecular structures. Most are nearly quantitative from the amine–aminocarbonyl compound complex stage. One of the special virtues in the use of an inert metal ion as a protecting group is that it will function as such over a wide pH range and ligands can thus organize intramolecular reactions under quite extreme conditions. The fact that highly reactive amido groups can be readily exposed on cobalt(III) is, of course, a form of very simple pH-dependent deprotection of amines.

**Acknowledgment.** The assistance of the ANU Microanalytical Unit is gratefully acknowledged.

**Registry No.** tren, 4097-89-6; trenpnim, 117228-98-5; trenphenol, 117228-99-6; trenphenim, 117229-00-2; trien, 112-24-3; Metetraenim, 117229-02-4; $[Co(tren)Cl_2]Cl$, 20023-19-2; $\alpha$-$[Co(trien)Cl_2]Cl$,

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(50) pD values were estimated from observed pH meter readings by using pD = $pH_{obs}$ + 0.40. See: Glasoe, P. K.; Long, F. A. *J. Phys. Chem.* **1960**, *64*, 188.

(51) Hawkins, C. J. *Absolute Configuration of Metal Complexes*; Wiley: New York, 1971; pp 63–86.

*Inorg. Chem.* **1988**, *27*, 4563–4566 **4563**

117229-22-8; $C_6H_4CO(CO)NCH_2COCH_3$, 3416-57-7; *p*-[Co(tren)-$\{NH_2CH_2CH(OH)_2\}$Cl]Cl($ClO_4$), 52675-78-2; $H_2NCH_2CH(OC_2H_5)_2$, 645-36-3; [Co(tren)$Cl_2$]$ClO_4$, 33393-50-9; *p*-[Co(tren)$\{NH_2CH_2$-$(CH_3)COCH_2CH_2O)$Cl]$(ClO_4)_2$, 117229-04-6; *p*-[Co(tren)-$(NH_2CH_2COCH_3)$Cl]$(ClO_4)_2$, 117229-06-8; *i*-[Co(trenpnim)Cl]$(ClO_4)_2$, 117229-08-0; $NH_2CH_2COCH_3$, 298-08-8; *s*-(*SR*,*RS*)-[Co(trenpn)Cl]-$(ClO_4)_2$, 117229-10-4; *p*-[Co(tren)$(NH_2CH_2CH(C_6H_5)OH)$Cl]$(ClO_4)_2$, 117229-12-6; *p*-[Co(tren)$(H_2NCH_2COC_6H_5)$Cl]$(ClO_4)_2$, 117229-14-8; $H_2NCH_2COC_6H_5$, 613-89-8; *s*-[Co(trenphenol)Cl]$(ClO_4)_2$, 117229-16-0; *i*-[Co(trenphenim)Cl]$(ClO_4)_2$, 117229-18-2; *s*-[Co(trenphen)Cl]$(ClO_4)_2$, 117229-20-6; *β*-*p*-Δ(*R*),Λ(*S*)-(Co(trien)$(H_2NCH_2CH(OCH_2CH_3)_2)$-Cl]$Br_2$, 117229-21-7; *β*-*p*-(*RR*)(*SS*)-[Co(trien)$(H_2NCH_2CH(OH)_2)$-Cl]$Cl_2$, 117229-23-9; *αβ*-*i*-[Co(tetraenim)Cl]$(ClO_4)_2$, 117229-25-1; $H_2NCH_2CH(OH)_2$, 117229-01-3; *αβ*-Δ(*S*),Λ(*R*)-[Co(tetraen)Cl]$^{2+}$, 16961-56-1; *αβ*-Δ(*R*),Λ(*S*)-[Co(tetraen)Cl]$^{2+}$, 117306-66-8; *αβ*-*i*-[Co-(tetraenim)$NO_2$]$ZnCl_4$, 117229-27-3; *αβ*-*p*-[Co(tetraenim)Cl]$(ClO_4)_2$, 117306-68-0; *αβ*-Δ(*S*),Λ(*R*)-[Co(tetraen)$NO_2$]$^{2+}$, 117306-69-1; *αβ*-Δ-(*R*),Λ(*S*)-[Co(tetraen)$NO_2$]$^{2+}$, 117306-70-4; *α*-[Co(trien)$\{H_2NCH_2$-$(CH_3)C(OCH_2CH_2O)\}$Cl]$Br_2$, 117229-28-4; *α*-[Co-(trien)$(H_2NCH_2COCH_3)$Cl]$(ClO_4)_2$, 117229-30-8; *αβ*-*s*-[Co(Metetraenim)Cl]$(ClO_4)_2$, 117229-32-0; [Co(Metetraen)Cl]$(ClO_4)_2 \cdot H_2O$ (isomer T), 117229-35-3; [Co(Metetraen)Cl]$(ClO_4)_2$ (isomer N), 117306-72-6; *αβ*-*s*-[Co(Metetraenim)$NO_2$]$ZnCl_4$, 117229-37-5; *αα*-[Co(tetraen)Cl]$^{2+}$, 16961-55-0; potassium phthalimide, 1074-82-4; chloroacetone, 78-95-5; 2-(phthalimidomethyl)-2-methyl-1,3-dioxolane, 1775-18-4; ethane-1,2-diol, 107-21-1; 2-methyl-2-(aminomethyl)-1,3-dioxolane, 3289-19-8.

**Supplementary Material Available:** Listings of anisotropic thermal parameters (Tables SUP-1 and SUP-2), hydrogen atom parameters (Tables SUP-3 and SUP-4), ligand and anion geometries (Tables SUP-5–SUP-7), ligand string torsion angles (Table SUP-8), and cyclization (Table SUP-9) and carbinolamine dehydration rate constants (Table SUP-10) (13 pages); listings of observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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# Kinetics and Mechanism of the Oxidation of 2,3-Dihydroxybenzoic Acid by Iron(III)

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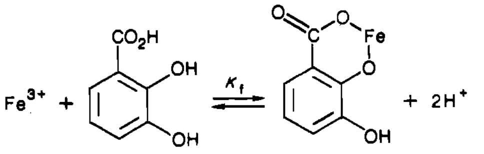
*Received November 23, 1987*

The kinetics of the oxidation of 2,-3-dihydroxybenzoic acid (DHB) by aqueous iron(III) have been studied in aqueous acid with [Fe(III)] ≫ [DHB]. The initial complexation reaction of $Fe(OH_2)_6^{3+}$ and DHB was studied previously. The iron(III)–DHB complex is oxidized by iron(III) with a rate law that is first order in iron(III) and has terms that are inverse first order in [$H^+$] and inverse second order in [$Fe(OH_2)_6^{2+}$]. It is shown that the oxidation does not proceed by simple intramolecular electron transfer within the iron(III)–DHB complex. A mechanism is proposed in which the latter complex reacts first by substitution on free iron(III) followed by two reversible electron-transfer steps to give the quinone product.

## Introduction

In a previous paper[1] it was reported that, in acidic aqueous solution, 2,3-dihydroxybenzoic acid (DHB) reacts with hexaaquairon(III) in three stages. The initially colorless solution turns blue and then yellow within a few minutes and finally brown after several hours. The colorless to blue stage was identified with the formation of an iron(III)–DHB complex as shown in eq 1. The equilibrium constant for eq 1 was found to be 7.0 M (25 °C, 1 M $NaClO_4$, $HClO_4$). The magnitude of the equilibrium constant was found to be most consistent with the salicylate mode of complexation shown in eq 1. The kinetics of the complexation reaction were reported previously.[1]



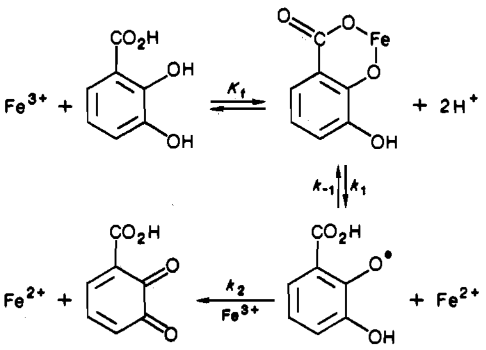
(1)

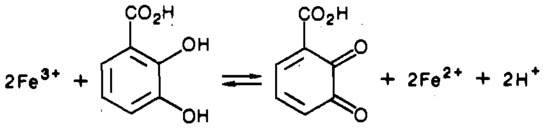
A kinetic study of the second stage of the reaction (blue to yellow) is reported here. It is shown that iron(II) is produced during this stage so that it is an oxidation–reduction process. This is expected from other studies which have shown that 1,2-dihydroxybenzene systems are oxidized to the corresponding quinone by hexaaquairon(III)[2,3] and other oxidizing agents.[4]

## Results and Discussion

A study of the reaction stoichiometry under conditions of [Fe(III)] ≫ [DHB] shows that 2 mol of iron(II) are produced/mol of DHB initially present. These observations are consistent with the overal oxidation of DHB to the quinone as shown in eq 2.

Scheme I





(2)

The blue to yellow color change that accompanies the reaction is observed spectrophotometrically as a decrease in absorbance in the region of the initial 600-nm maximum, with a corresponding increase in absorbance at 400 nm and an isosbestic point at 506 nm. The reaction kinetics have been studied as a function of the concentration of iron(III), iron(II) and $H^+$, always with [Fe(III)] ≫ [DHB]. The results are summarized in Table I.

Under the concentration conditions of this study, the complexation reaction (eq 1) is known[1] to be at least 25 times faster than the redox reaction. Therefore the complexation can be viewed as a rapid preequilibrium. It should be noted also that the DHB is more than 95% complexed for all but 6 of the 28 different concentration conditions listed in Table I.

The first 11 runs in Table I show that the apparent pseudo-first-order rate constant ($k_{obsd}$) decreases as the [$H^+$] increases.

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(1) Xu, J.; Jordan, R. B. *Inorg. Chem.* **1988**, *27*, 1502.

(2) Mentasti, E.; Pelizzetti, E.; Saini, G. *J. Chem. Soc., Dalton Trans.* **1973**, 2604.

(3) Mentasti, E.; Pelizzetti, E.; Barocchi, C. *J. Inorg. Nucl. Chem.* **1976**, *38*, 2017.

(4) (a) Pelizzetti, E.; Mentasti, E. *Z. Phys. Chem. (Munich)* **1977**, *105*, 21. (b) Pelizzetti, E.; Mentasti, E.; Barocchi, C. *J. Phys. Chem.* **1976**, *80*, 2979. (c) Macartney, D. H.; McAuley, A. *J. Chem. Soc., Dalton Trans.* **1984**, 103.

0020-1669/88/1327-4563$01.50/0