spectrum identical with that of the original *trans* compound.

Studies using the *cis-β* isomer for hydrolysis of small polypeptides will be reported elsewhere.

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Cobalt(III) Complexes of Linear Tetramines. III. Complexes of 4,7-Diaza-1,10-decanediamine[1]

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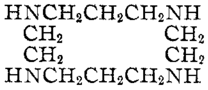
Cobalt(III) complexes of the new tetramine ligand, 4,7-diaza-1,10-decanediamine, $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$ (3,2,3-tet), have been prepared and characterized. One of these, *trans*-$Co(3,2,3\text{-tet})Cl_2^+$, aquates in acidic solution with retention of topology to yield *trans*-$Co(3,2,3\text{-tet})(H_2O)Cl^{2+}$: $\Delta H^{\ddagger} = 24.5$ kcal mol^{-1}; $\Delta S^{\ddagger} = +4$ cal deg^{-1} mol^{-1}. Carbonate ion reacts with *trans*-$[Co(3,2,3\text{-tet})Cl_2]ClO_4$ in aqueous media to produce $[Co(3,2,3\text{-tet})CO_3]ClO_4$. Unlike other carbonato(tetramine)cobalt(III) complexes, $[Co(3,2,3\text{-tet})CO_3]ClO_4$ reacts with concentrated hydrochloric acid to yield *trans*-$Co(3,2,3\text{-tet})Cl_2^+$ rather than a *cis* isomer.

Introduction

Much activity has been in evidence recently concerning the study of cobalt(III) complexes of branched and nonbranched linear tetramines. The stereochemistry of such complexes is extremely interesting for many reasons among which are the interplay of the three stereochemical factors: over-all topology (*trans*, *cis-β*, and *cis-α* structures, Figure 1), asymmetric sites on the ligand (carbon atoms in the case of branched tetramines and secondary amine functions), and chelate ring conformations. The two nonbranched tetramines which have been investigated to date, triethylenetetramine, $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$ (trien), and 3,7-diaza-1,9-nonanediamine, $NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$ (2,3,2-tet), differ only in the linkage between ethylenediamine moieties—ethylene linkage for trien and trimethylene linkage for 2,3,2-tet. The increased flexibility and length of trimethylene relative to an ethylene linkage have been found to give rise to a considerable difference in the coordination stereochemistries of these two ligands. For example, *cis* topologies are preferred for trien complexes while *trans* topologies are generally preferred for 2,3,2-tet complexes.[2-5] Furthermore, the configurations of the two asymmetric secondary amine functions are much more dependent upon each other in the trien case than in the case of 2,3,2-tet. Both of these differences can be easily explained in terms of the length and flexibility of the bridging moieties.

In extending our work with complexes of linear tetramines we have prepared some cobalt(III) complexes of 4,7-diaza-1,10-decanediamine, $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$ (3,2,3-tet). This nonbranched tetramine resembles the two aforementioned: the central bridging moiety is an ethylene function but trimethylene moieties join the terminal amines with the secondary amine groups. The relationship between the two linear tetramines 3,2,3-tet and 2,3,2-tet and the macrocyclic ligand 1,4,8,12-tetraazacyclotetradecane (I),



I

the complexes of which are attracting increasing attention,[6] provides added interest in these linear tetramines. The preparation of some 3,2,3-tet complexes of cobalt(III) and stereochemical studies on these complexes are presented in this paper.

Experimental Section

Preparation of 4,7-Diaza-1,10-decanediamine.—The procedure employed in the preparation of this ligand is analogous to that described for preparation of 2,3,2-tet.[4] To a cold, constantly stirred solution of 1,2-dibromoethane (272 g) in ethanol (500 ml) was added 1,3-diaminopropane (585 g). The solution was warmed to 50° for 1 hr. Solid KOH (400 g) was added slowly, and the mixture was warmed another 0.5 hr. After filtering to remove KBr, the remaining 1,2-dibromoethane, 1,3-diaminopropane, and ethanol were removed by distillation. The solution was then cooled, filtered, and fractionally distilled under vacuum using a Todd 12.5-mm glass-packed fractionation column. The desired product was collected at 135–137° at a pressure of 1.5–2 mm; yield, 40 g.

Preparation of *trans*-Dichloro(4,7-diaza-1,10-decanediamine)-cobalt(III) Perchlorate.—An aqueous solution (300 ml) containing $CoCl_2 \cdot 6H_2O$ (11.5 g) and 3,2,3-tet (8.0 g) was air oxidized

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[1] From the Ph.D. thesis of H. G. H., New Mexico State University, June 1968.

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[4] H. G. Hamilton and D. Alexander, *Inorg. Chem.*, **5**, 2060 (1966).

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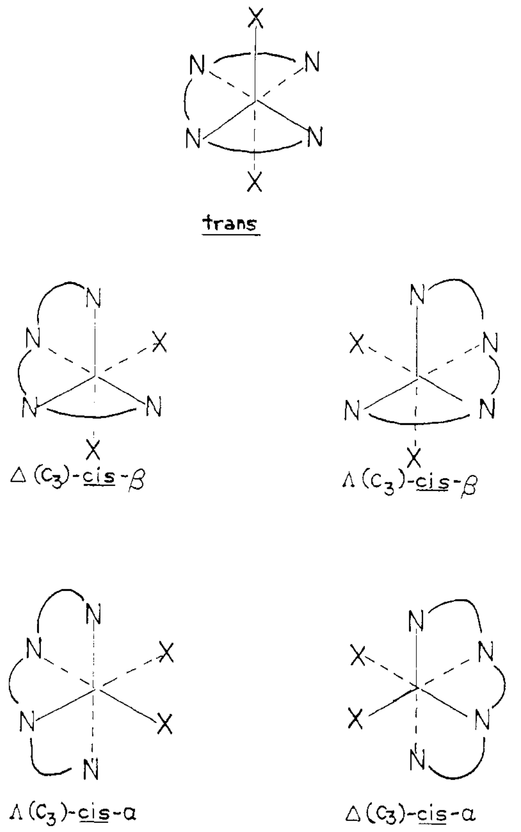

Figure 1.—Possible topologies of the $Co(tet)X_2^{n+}$ ion.

for a period of 12 hr. With addition of concentrated hydrochloric acid (20 ml), the solution became yellow-green. Upon evaporation on a steam bath to a volume of approximately 200 ml, a green solid material began to form. This material was collected, washed with cold water and ethanol, and air dried. However, chloride analysis was not consistent with the formulation $[Co(3,2,3\text{-tet})Cl_2]Cl$. The green material was therefore dissolved in concentrated hydrochloric acid and precipitated as the perchlorate salt using $HClO_4$. The product was then removed by filtration, washed with water, ethanol, and ether, and dried *in vacuo* at 100° overnight; yield, 7 g. *Anal.* Calcd for $[Co(C_8H_{22}N_4)Cl_2]ClO_4$: C, 23.80; H, 5.49; N, 13.89. Found: C, 23.65; H, 5.40; N, 13.73. The aqueous molar conductivity was 109 $ohm^{-1}\ cm^2\ mol^{-1}$.

Preparation of Carbonato(4,7-diaza-1,10-decanediamine)-cobalt(III) Perchlorate.—Five grams of *trans*-$[Co(3,2,3\text{-tet})Cl_2]ClO_4$ was partially dissolved in water (25 ml) after which solid Na_2CO_3 (5.0 g) was added with constant stirring. The mixture was heated on a steam bath for 0.5 hr and then cooled in an ice bath. Following filtration, ice-cold methanol was carefully added to induce crystallization of the desired material. The pink needles which formed were recrystallized from water–methanol, washed with methanol and ether, and dried *in vacuo* at 50° overnight; yield, 3 g. *Anal.* Calcd for $[Co(C_8H_{22}N_4)CO_3]ClO_4$: C, 27.60; H, 5.65; N, 14.30. Found: C, 27.82; H, 5.90; N, 14.28. The aqueous molar conductivity was 90 ohm^{-1} $cm^2\ mol^{-1}$.

Reaction between Carbonato(4,7-diaza-1,10-decanediamine)-cobalt(III) Perchlorate and Hydrochloric Acid.—Concentrated hydrochloric acid (15 ml) was added to $[Co(3,2,3\text{-tet})CO_3]ClO_4$ (1 g). Carbon dioxide was evolved and a color change from the red of the carbonato complex to the green of the product was observed in just a few seconds. Sparingly soluble *trans*-$[Co(3,2,3\text{-tet})Cl_2]ClO_4$ began to crystallize in a short time. These crystals were filtered, washed with methanol, and air dried.

Infrared Spectra.—Infrared data were obtained using a Beckman IR-8 spectrophotometer. Nujol mulls were employed in determining these spectra.

Elemental Analyses.—Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Chloride analyses were accomplished through a potentiometric titration using a Beckman expandomatic pH meter equipped with silver wire and saturated calomel electrodes. Solutions were adjusted to pH 8 with 0.01 *N* NaOH for chloride titrations. A standard $AgNO_3$ solution was used as the titrant.

Conductivity Measurements.—Conductivity measurements were performed using an Industrial Instruments Model 16B2 conductivity bridge. Molar conductivities were determined at 25° in aqueous solution at a concentration of $1.00 \times 10^{-3}\ M$.

Visible Absorption Spectra.—Visible absorption spectra were determined using a Beckman DB spectrophotometer equipped with a recorder. Standard 1- and 4-cm silica cells were used. Visible spectra measurements were made on aqueous solutions immediately after preparation to eliminate problems of hydrolysis.

Kinetic Measurements.—Two methods were employed in determining the aquation rates for the first chloride replacement in *trans*-$[Co(3,2,3\text{-tet})Cl_2]Cl$. The first of these techniques relied upon the change in absorbancy at 306 mμ with formation of the chloroaquo species. A weighed sample of approximately 10 mg of complex was dissolved in 100 ml of 0.010 *N* $HClO_4$ which had previously been equilibrated to the desired temperature. This solution was then maintained in a constant-temperature bath and at appropriate time intervals aliquots were withdrawn for spectral measurements using a Beckman DB spectrophotometer equipped with a thermostated cell compartment and 1-cm silica cells. Rate data were obtained at 25, 35, and 45°.

Aquation rate data were also obtained through determination of the rate of chloride ion release. Weighed samples of approximately 0.2 g of complex were dissolved in 100 ml of 0.010 *N* HNO_3 which had been equilibrated to 25°. These solutions were maintained at 25° and at appropriate time intervals 10-ml aliquots were removed and quickly absorbed on a Dowex 50W-X2-ion-exchange column which had been washed several times with deionized water. Cationic species were absorbed on the column, while the chloride-containing effluent was collected and titrated with standard $AgNO_3$.

Mercury(II)-Assisted Aquation.—*trans*-$[Co(3,3,3\text{-tet})Cl_2]Cl$ (3.25 g) was dissolved with stirring in approximately 100 ml of water. A second solution was prepared by dissolving $Hg(NO_3)_2$ (3.43 g) in a similar volume of water to which 1 ml of concentrated HNO_3 had been added. These solutions were then rapidly mixed, and the resulting solution was stirred for 10 min. The solution was then passed through a Dowex 50W-X2 cation-exchange column. Elution of the cationic species absorbed on the column was accomplished using 1 *N* HNO_3. Unreacted *trans*-$Co(3,2,3\text{-tet})Cl_2^+$ passed through the column, rapidly. The second band to pass through the column was identified to be *trans*-$Co(3,2,3\text{-tet})(H_2O)Cl^{2+}$ *via* its visible absorption spectral similarity to *trans*-$Co(en)_2(H_2O)Cl^+$ (λ_{max} 607 mμ for 3,2,3-tet complex and λ_{max} 590 mμ for the $(en)_2$ complex). A third band, consisting of tripositive diaquo species, was eluted much more slowly than the second.

Results and Discussion

The preparation of *trans*-dichloro-(4,7-diaza-1,10-decanediamine)cobalt(III) perchlorate is carried out in the same fashion as the corresponding 2,3,2-tet complex, *i.e.*, *via* the common air-oxidation technique. Elemental analysis and molar conductivity are in accord with the formulation. The *trans* topology is assigned to the 3,2,3-tet complex on the basis of its visible spectral similarity with *trans*-$Co(2,3,2\text{-tet})Cl_2^+$ and *trans*-$Co(en)_2Cl_2^+$ (Figure 2) as well as with other *trans* dichloro(tetramine)cobalt(III) complexes.

In acidic aqueous solution *trans*-$Co(3,2,3\text{-tet})Cl_2^+$ undergoes relatively rapid aquation with retention of

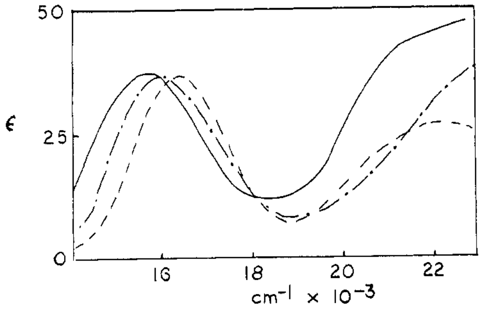

Figure 2.—Visible spectra of *trans*-Co(3,2,3-tet)Cl_2^+ (—), *trans*-*RR,SS*-Co(2,3,2-tet)Cl_2^+ (—·—), and *trans*-Co(en)$_2Cl_2^+$ (— —).

topology to produce *trans*-Co(3,2,3-tet)(H_2O)Cl^{2+}, identified *via* its visible spectrum (λ_{max} 607 mμ). Plots of log $|A_t - A_\infty|_{306m\mu}$ (A_t and A_∞ are the absorptions at time t and after 8 half-lives, respectively, measured at 306 mμ) were found to be linear. First-order rate constants obtained from these plots and also from a chloride-titration technique are given in Table I. The Arrhenius plot of log k *vs.* $1/T$ yields the activation parameters shown in Table II. Also shown are those for the same reaction of analogous complexes.

TABLE I

RATE CONSTANTS FOR AQUATION OF *trans*-Co(3,2,3-tet)Cl_2^+ (pH 2; μ = 0.01)

Temp, °C	k, min^{-1}	Temp, °C	k, min^{-1}
25	3.18×10^{-3} [a]	35	1.26×10^{-2} [a]
	3.39×10^{-3} [b]	45	4.78×10^{-2} [a]

[a] From spectral technique. [b] From chloride-titration technique.

TABLE II

ACTIVATION PARAMETERS AND TOPOLOGICAL COURSE FOR THE REACTION

$$trans\text{-Co(tet)Cl}^+ + H_2O \longrightarrow \text{Co(tet)(H}_2\text{O)Cl}^{2+} + Cl^-$$

tet	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, deg^{-1} mol^{-1}	% topological change	Ref
3,2,3-tet	24.5	+4	0	
RS-2,3,2-tet	24.6	+1	0	1
RR,SS-2,3,2-tet	24.7	+9	100	1

Tobe[7] has noted that for aquation reactions of *trans*-chloroacidocobalt(III) complexes in (en)$_2$, trien, 2,3,2-tet, and cyclam systems in which no topological change occurs, entropies of activation are negative while for those reactions in which topological change does occur $\Delta S^\ddagger$ is positive. Furthermore, Tobe has suggested that higher entropies of activation are indicative of dissociative processes proceeding through trigonal-bipyramidal five-coordinate intermediates and that lower entropies of activation (negative) are indicative of tetragonal-pyramidal intermediates. This conclusion is based, in part, upon the notion that trigonal-bipyramidal intermediates may lead to topological change and that tetragonal-pyramidal species lead to no such change.

The data for the 3,2,3-tet system are seen to be in exception to the general trend; that is, the aquation reaction occurs with a positive $\Delta S^\ddagger$ and results in no topological change. The data can be rationalized easily, however. The positive $\Delta S^\ddagger$ is indicative of a loosening of the structure in the activated complex for the rate-determining step, the chloride expulsion. This could be accomplished without a major rearrangement of the tetramine ligand. For example, if the intermediate in the 3,2,3-tet case were to have a slightly distorted tetragonal-pyramidal structure such that a greater flexibility of the ligand could be assumed, then retention of topology and a positive $\Delta S^\ddagger$ would be observed provided some of this increased flexibility is realized in the activated complex.

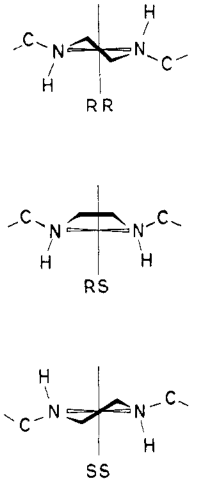

Figure 3.—Possible secondary nitrogen configurations for *trans*-Co(3,2,3-tet)Cl_2^+.

It is interesting to note that the enthalpies of activation for the aquation of *trans*-Co(3,2,3-tet)Cl_2^+, *trans*-*RS(meso)*-Co(2,3,2-tet)Cl_2^+, and *trans*-*RR,SS*-Co(2,3,2-tet)Cl_2^+ are the same within experimental error (Table II) even though no topological change occurs for the former two but complete change occurs for the latter complex. These data appear to be contrary to Tobe's notion that for a topological change to occur during the aquation reaction the tetramine must undergo a major rearrangement in forming the activated complex for the rate-determining chloride expulsion.[7] Such a rearrangement would surely have a noticeable effect on $\Delta H^\ddagger$. Thus, it appears that the major rearrangement of the tetramine occurs subsequent to the formation of the five-coordinate intermediate.

To this point nothing has been said concerning the configurations of the asymmetric secondary nitrogen atoms in *trans*-Co(3,2,3-tet)Cl_2^+. As in the case of the analogous trien and 2,3,2-tet complexes, *RS(meso)*, *RR*, and *SS* configurations are possible. The first-order kinetic data for the aquation reaction strongly indicate that the complex is either the *RS(meso)* isomer or the *RR,SS* racemate and not a mixture of the diastereomers since the *RS(meso)* isomer should aquate at a different rate than the *RR,SS* racemate.

As can be seen in Figure 3, for the *RS(meso)* case, the ethylene moiety in 3,2,3-tet must assume the eclipsed envelope conformation while for the *RR* and *SS* con-

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[7] M. L. Tobe, *Inorg. Chem.*, **7**, 1260 (1968).

figurations the *gauche* conformation must be assumed. For a chelated ethylenediamine molecule the eclipsed conformation has been shown to be less stable than the *gauche* conformation.[8,9] Furthermore, in the case of trien, the *RR* and *SS* antipodes of *trans*-Co(trien)Cl_2^+, in which the ethylene moiety bridging the secondary amine is *gauche,* are more stable than the *RS*(*meso*) isomer, in which the ethylene is eclipsed.[2] Thus, one might predict that *trans*-[Co(3,2,3-tet)Cl_2]ClO_4 is most probably the *RR,SS* racemate. One piece of experimental evidence lends support to this notion. If this complex is subjected to Hg^{2+}-induced aquation (reaction 1), only one *trans*-chloroaquo product can be isolated *via* cation-exchange chromatography. Since in this reaction no nitrogen configurational change should occur because of the strongly acidic condition,[2-4] the product should have the same configuration as the reactant. Two isomers of this product are predicted for the *RS*(*meso*) case because of the nonequivalence of *trans* sites while for both the *RR* and *SS* configurations no such geometrical isomerism is possible. For the aquation of the analogous *trans-RS*(*meso*)-Co(2,3,2-tet)Cl_2^+ two such *trans-RS*(*meso*)-chloroaquo complexes are produced and separated *via* cation-exchange chromatography under conditions identical with those employed for the 3,2,3-tet case.[3] It would seem most likely that if *trans*-Co(3,2,3-tet)Cl_2^+ were the *RS*(*meso*) isomer, similar behavior would be observed.

$$\textit{trans}\text{-Co(3,2,3-tet)}Cl_2^+ + 0.5Hg^{2+} + H_2O \xrightarrow{H^+} \textit{trans}\text{-Co(3,2,3-tet)}(H_2O)Cl^{2+} + 0.5HgCl_2 \quad (1)$$

All attempts to prepare *cis*-Co(3,2,3-tet)Cl_2^+ proved unsuccessful. Only by use of a bidentate ligand to occupy *cis* sites were complexes of the *cis* topology prepared. Among these is *cis*-[Co(3,2,3-tet)CO_3]ClO_4. This compound, prepared by reaction of CO_3^{2-} with *trans*-Co(3,2,3-tet)Cl_2^+, was characterized *via* elemental analysis, molar conductivity, and its visible absorption spectrum (λ_{max} 520 mμ, ϵ 127; λ_{max} 360 mμ, ϵ 125). As to whether the complex exhibits the α or β topology, there is no direct evidence. However, the apparent stability of *trans* structures in 3,2,3-tet systems suggests the β topology.

The carbonato complex undergoes hydrolysis in hydrochloric acid to yield *trans*-[Co(3,2,3-tet)Cl_2]ClO_4. This behavior is in contrast to that of β-Co(trien)CO_3^+ and β-Co(2,3,2-tet)CO_3^+, both of which yield *cis*-β-dichloro products.[1,2] The *trans*-[Co(3,2,3-tet)Cl_2]ClO_4 complex prepared from the carbonato complex exhibits an infrared spectrum indistinguishable from that of the complex prepared *via* the air-oxidation technique. No secondary nitrogen configuration change is expected in the acid hydrolysis of Co(3,2,3-tet)CO_3^+.[2-4] Thus, the indication is that no nitrogen configurational change occurs in the reaction of CO_3^{2-} and *trans*-Co(3,2,3-tet)Cl_2^+ even though such change is possible under the basic conditions of the reaction.

At this point let us summarize some of the stereochemical properties of 3,2,3-tet with respect to other tetramine systems. The ligand 3,2,3-tet coordinates to cobalt(III) preferably with the *trans* topology. This behavior is unlike that of trien, for which *cis* topologies are preferred, but is similar to that of 2,3,2-tet as well as the macrocyclic tetramine cyclam.[5] The complex *trans*-Co(3,2,3-tet)Cl_2^+ aquates with retention of topology as does *trans-RS*(*meso*)-Co(2,3,2-tet)Cl_2^+ but not as do *trans-RR,SS*-Co(trien)Cl_2^+ and *trans-RR,SS*-Co(2,3,2-tet)Cl_2^+, both of which yield *cis*-β-chloroaquo products.[1-5]

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