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Synthesis of a New Triethylenetetramine Homolog Containing Four Optically Pure Centers. Some Stereoselective Cobalt(III) Ion Complexes of This Ligand

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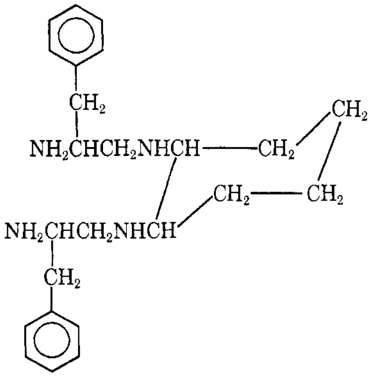
The synthesis of a new tetramine ligand, a homolog of triethylenetetramine which contains four optical centers, is reported. It is N,N′-bis(L-2-amino-3-phenylpropyl)-*trans*-D-1,2-cyclohexanediamine. The syntheses of the L-*cis*-β- and optically active *trans*-cobalt(III) perchlorate derivatives are reported. Absorption and optical rotatory dispersion spectra are reported and used, along with some chemical data, to assign the configurations of the isomer.

During the past 10 years a lot of work has been done related to stereoselective polydentate ligands.[2] Included among them are various optically active polyamines,[3] for example, D-pn, L-chxn, LL-α,α′-dimethyltrien,[4a,b] LL-β,β′-dimethyltrien,[4c] N,N-2-picolyl-1-methyl-1,2-diaminoethane.[4d]

For the optically active diamines such as L-propylenediamine, the distribution of tris(diamine)cobalt(III) ion isomers is essentially that predicted by Corey and Bailar.[5a] These workers also predicted an increase in stability of 2 kcal/mol for the chelated ring conformation having the substituent group equatorial rather than axial.[5b-d] No similar semiquantitative theoretical study has been done for the tetramines, but some qualitative predictions of yield and configuration were borne out in the case of $Co(LL\text{-}\alpha,\alpha'\text{-}(CH_3)_2trien)Cl_2^+$ ionic products.[4a] The complex, however, easily isomerized under certain reaction conditions.[6]

In the interest of chemical reaction simplicity, it would be desirable to have a polyamine ligand which would coordinate with the cobalt(III) ion in a stereoselective manner but without the possibility of complicating isomerizations. Toward these ends, we have initiated studies to synthesize such polyamine ligands.

This paper will report on the synthesis and stereoselective coordination to the cobalt(III) ion of the new tetramine ligand abbreviated here as LDDL. This ligand is best viewed as a homolog of triethylenetetramine with four optically active carbons. Our work was initiated in order to find a polyamine ligand which would be absolutely stereospecific, and it was anticipated that this particular ligand would coordinate stereoselectively with the cobalt(III) ion. It was not possible to predict with certainty the isomers which would form, but knowledge concerning the LL-α,α′-$(CH_3)_2$trien ligand led us to anticipate that the symmetrical D-*cis*-α isomer would be the most stable for the following reason. The backbone of the cobalt *cis*-α isomer with LL-α,α′-$(CH_3)_2$trien has a conformation opposite to that assumed by the two arms, both of which have the same conformation. Thus, if the arms are in the k conformation, the backbone would be most stable in the k′ conformation. It was expected that the arms of LL-α,α′-$(CH_3)_2$trien would be in the k conformation because the configuration of their optically active carbons is L (relative to L-alanine). In absolute configuration they are *S*.[7] Their methyl groups would be equatorial in the k conformation and axial in the k′ conformation. Thus, any optically active backbone carbons should have the configuration D in order to give the more stable conformation to that chelated ring. If the backbone were propylenediamine, its D isomer would have k′ as the more stable conformation as would *trans*-cyclohexanediamine.



LDDL

The relative configurations of the optically active diamines have been deduced[8] to be: L-alanine = (+)-propylenediamine = (+)butylenediamine = (+)cyclopentanediamine = (+)cyclohexanediamine = (−)-stilbenediamine, where (+) refers to the sign of the rotation at 5890 Å. Thus, we reasoned that the configurational order along the chain should be D in the

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[2] For a recent review, see R. D. Gillard, *Inorg. Chim. Acta*, **1**, 69 (1967).

[3] Abbreviations used in this paper are: D-pn, D-propylenediamine; L-chxn, L-cyclohexanediamine; LL-α,α′-$(CH_3)_2$trien, 2,9-diamino-4,7-diazadecane; LL-β,β′-$(CH_3)_2$trien, 1,8-diamino-2,7-dimethyl-3,6-diazaoctane; LDDL, N,N′-bis(L-2-amino-3-phenylpropyl)-*trans*-D-1,2-cyclohexanediamine.

[4] (a) R. G. Asperger and C. F. Liu, *Inorg. Chem.*, **4**, 1397 (1965); (b) R. G. Apserger and C. F. Liu, *ibid.*, **6**, 796 (1967); (c) S. Yoshikawa, T. Sekihara, and M. Goto, *ibid.*, **6**, 169 (1967); (d) B. Bosnich, *Proc. Roy. Soc.* (London), **A297**, 88 (1967).

[5] (a) E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959); (b) R. D. Gillard, *Inorg. Chim. Acta*, **1**, 69 (1967); (c) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **81**, 1043 (1959); (d) F. P. Dwyer, F. L. Garvan, and A. Shulman, *ibid.*, **81**, 290 (1959), and other later papers by Dwyer, *et al.*

[6] R. G. Asperger and C. F. Liu, *ibid.*, **89**, 908, 1533 (1967).

[7] See K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 96.

[8] R. D. Gillard, *Tetrahedron*, **21**, 503 (1965); (b) J. H. Dulop, R. D. Gillard, and H. Wilkinson, *J. Chem. Soc.*, 3160 (1964), and references therein; (c) F. Woldbye, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **24**, 197 (1963).

backbone, with L absolute configurations in the arms if a stable *cis*-α isomer were to be obtained. This analysis was based only on a qualitative conformational analysis using space-filling molecular models. Although the same type of analysis predicted the isomeric distribution for the $Co(LL\text{-}\alpha,\alpha'\text{-}(CH_3)_2trien)CO_3^+$ ion, it was not successful with the complex $Co(LDDL)Cl_2^+$ for which the most stable isomer was observed to be *trans* not *cis*-α. With extreme care, the *cis*-β isomer could also be isolated.

Experimental Section

Optical rotatory dispersion measurements were made in 1-cm cells at 25 ± 2° on a Cary 60 spectropolarimeter.

Infrared spectra were taken on a Perkin-Elmer Model 137 ir spectrometer using Nujol mulls.

Elemental analyses were performed by Dr. Leroy Swim, Microanalytical Laboratories, The Dow Chemical Co.

Chemicals used were commercial reagent grade except for *trans*-cyclohexanediamine which was purchased as the sulfate salt from Aldrich Chemical Co., and L-phenylalanine which was purchased from Nutritional Biochemicals Co.

Preparation of L-Phthaloylphenylalanine.—An intimate 1:1 molar mixture of L-phenylalanine and phthalic anhydride was heated to 150° until completely molten and was maintained at that temperature for 3 hr. The mixture was then cooled and the solid dissolved in a minimal amount of hot absolute alcohol. The product was obtained on standing at 0° for 8 hr followed by recrystallization by the same method; mp 185–185.5°; yield 50%.

Measurement of the ORD spectrum in the region of the uv Cotton effect, at 240–200 mμ, showed that the consecutive fractions were identical. Thus, the product was optically pure.

Anal. Calcd for $C_{17}H_{13}NO_4$: C, 69.1; H, 4.44; N, 4.74. Found: C, 69.4; H, 4.49; N, 4.75.

Preparation of L Phthaloylphenylalanine Acid Chloride.— To 450 ml of benzene at 55° was added 29.5 g (0.1 mol) of L-phthaloylphenylalanine followed by the slow addition of 20.8 g (0.1 mol) of PCl_5 during 15 min. This solution was heated for 1 hr at 55° and then stripped of solvent under reduced pressure. The product was dried under continuous high vacuum for 8 hr before use. It was not further characterized.

Preparation of D-Diaminocyclohexane Dihydrochloride.—D-Diaminocyclohexane dihydrochloride was prepared according to the method of Asperger and Liu.[9a] The materials used were pure hand-picked crystals with $[M]^{25}D$ −29.6° in water. Baldwin[9b] has shown that for 1,2-diaminocyclohexane the sign of rotation is the same for the free amine and the mono- and the dihydrochloride. Thus (−)chxn·2HCl has the D absolute configuration.[8c]

Preparation of N,N′-Bis(phthaloyl-L-phenylalanyl)-DD-1,2-diaminocyclohexane.—To an ice-cold aqueous solution containing 9.35 g (0.05 mol) of D-diaminocyclohexane dihydrochloride, 4.2 g (0.10 mol) of lithium hydroxide hydrate, and 8.4 g (0.10 mol) of sodium bicarbonate was slowly added 31.37 g (0.10 mol) of L-phthaloylphenylalanine acid chloride dissolved in 130 ml of dry dioxane. The acid chloride was added dropwise while rapidly stirring and maintaining the solution at −5° in an ice–salt bath. After completing the addition, sufficient concentrated HCl was added dropwise to the two-phase system to decompose the excess bicarbonate. The oil phase was removed and dissolved in a minimal amount of hot 95% ethanol. Hot water was added to the filtered alcoholic solution to the oil point. Crystallization of the crude product was induced by scratching the side of the flask. The yield was 22.7 g or 68%. The product was recrystallized from ethanol; mp 258–259.5°.

Anal. Calcd for $C_{40}H_{36}N_4O_6$: C, 71.7; H, 5.28; N, 8.37. Found: C, 71.7; H, 5.56; N, 8.32.

Preparation of N,N′-Bis(L-phenylalanyl)-DD-1,2-diaminocyclohexane Dihydrochloride Hydrate.—A charge containing 10 g (0.015 mol) of N,N′-bis(phthaloyl-L-phenylalanyl)-DD-1,2-diaminocyclohexane and 150 ml of 1 *M* hydrazine in ethanol was prepared and diluted to 250 ml with ethanol. After refluxing for 5 hr the solvent was removed by distillation. The resulting residue was dried under high vacuum for 4 hr to dry the residue completely after which 50 ml of 2 *N* HCl was added. This mixture was maintained at 50° for 10 min with stirring followed by cooling to 5° and filtering. The product, which decomposed at 290–293°, was obtained in a yield of 95% by concentrating the solution at room temperature in a rotatory evaporator under reduced pressure.

Anal. Calcd for $C_{24}H_{32}N_4O_2 \cdot 2HCl \cdot H_2O$: C, 57.7; H, 7.27; N, 11.2; Cl, 14.2. Found: C, 57.5, 57.5; H, 7.25, 7.30; N, 11.2, 11.3; Cl, 14.35, 13.9.

Preparation of N,N′-Bis(L-2-amino-3-phenylpropyl)-DD-1,2-diaminocyclohexane Tetrahydrochloride Monohydrate, LDDL·4HCl·H₂O.—To 1 l. of an ice-cold 1 *M* $BH_3 \cdot THF$ adduct solution in THF was carefully added 9.8 g (2.18×10^{-2} mol) of N,N′-bis(L-phenylalanyl)-DD-1,2-diaminocyclohexane dihydrochloride hydrate. This solution was slowly heated to refluxing temperature and refluxed for 3 days. Then 150 ml of 1 *N* HCl solution was added dropwise to the hot, well-stirred solution. After drying the decomposed solution under reduced pressure or on a steam bath, the residue was treated with 50 ml of 20% NaOH. The freed amine was extracted into 300 ml of *n*-butyl alcohol. The aqueous phase was extracted with a second 300-ml batch of *n*-butyl alcohol. After adding HCl and evaporating the *n*-butyl alcohol solution to dryness, the residue was triturated with 200 ml of absolute alcohol. The product was obtained from the alcoholic filtrate by slowing adding ether during several hours until no further precipitation occurred. The yield of crude product was 70–75% for three preparations.

Anal. Calcd for $C_{24}H_{36}N_4 \cdot 4HCl \cdot H_2O$: C, 52.9; H, 7.78; N, 10.29; Cl, 26.05. Found: C, 52.7, 52.9; H, 7.86, 7.86; N, 10.29, 10.35; Cl, 25.7, 25.8.

Preparation of $Co(LDDL)Cl_2 \cdot 1.5H_2O$.—A solution was prepared which contained 0.544 g (10^{-3} mol) of $LDDL \cdot 4HCl \cdot H_2O$ (as prepared just above), 0.238 g (10^{-3} mol) of $CoCl_2 \cdot 6H_2O$ dissolved in 25 ml of H_2O and 5 ml of ethanol. This was aerated with CO_2-free air for 30 min using a filter stick to decrease the air bubble size. At this point the brown, alcohol-soluble crystals present in solution were removed by filtration. Yields varied from 1 to 10% and depended upon the per cent alcohol in solution. During most preparations, these crystals were redissolved into the solution by the addition of more ethanol.

Anal. Calcd for $C_{24}H_{36}N_4CoCl_2 \cdot 1.5H_2O$: C, 53.6; H, 7.33; N, 10.41. Found: C, 53.3, 53.4; H, 7.33, 7.40; N, 10.56, 10.54.

Preparation of L-*cis*-β-$(Co(LDDL)Cl_2)ClO_4 \cdot 3H_2O$.—The filtrate from the above compound was aerated as above for another 3 hr while adding enough alcohol from time to time to keep the mixture homogeneous. Then the solution was reduced to nearly one-fourth its original volume using moving air in a rotatory evaporator while maintaining the temperature at 30°. To this mixture of concentrated solution and brown precipitate was added 25 ml of concentrated HCl yielding a red product which was isolated by filtration using a fine sintered-glass filter; yield 97%. The solid was dissolved in a minimum amount of 95% ethanol and 0.5 ml of 70% perchloric acid was added. After standing for 12 hr at −10° in a freezing chest, a green product, yield 1–2%, was removed by filtration. The filtrate was evaporated nearly to dryness giving the L-*cis*-β product in 98–99% yield based on the yield of crude precipitate.

Anal. Calcd for $C_{24}H_{36}N_4O_4CoCl_3 \cdot 3H_2O$: C, 43.5; H, 6.37; N, 8.45; Cl, 16.05. Found: C, 43.6; H, 5.96, 6.08; N, 8.46; Cl, 15.8.

Preparation of *trans*-$(Co(LDDL)Cl_2)ClO_4$.—The green compound obtained above was believed to be the *trans* isomer.

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(9) (a) R. G. Asperger and C. F. Liu, *Inorg. Chem.*, **4**, 1492 (1965); (b) W. C. G. Baldwin, *Proc. Roy. Soc.* (London), **A167**, 539 (1938).

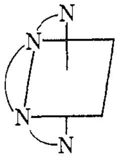
Anal. Calcd for $C_{24}H_{36}N_4O_4CoCl_3$: C, 47.26; H, 5.95; N, 9.19; Cl, 17.44. Found: C, 47.29; H, 5.94; N, 9.21; Cl, 18.2.

Preparation of L-*cis*-β-Co(LDDL)CO_3^+ *in Situ*.—A slight excess of $NaHCO_3$ was added to an aged aqueous solution of the L-*cis*-β-Co(LDDL)Cl_2^+ ion. After standing for several days, the desired product was obtained in solution. It was at this point that the ORD curve of the product was taken. See Figure 1.

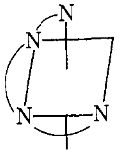
Preparation of L-*cis*-β-Co(LDDL)$(H_2O)_2^{3+}$ *in Situ*.—To the aged solution of the carbonate prepared just above was added 70% $HClO_4$ until the solution was slightly acid and CO_2 evolution stopped. The desired product was characterized by its ORD curve. See Figure 1.

Discussion

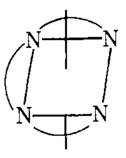
There are three possible geometrical isomers for the ligand triethylenetetramine in an octahedral complex.



cis-α



cis-β

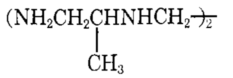


trans

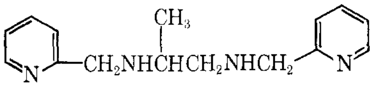
Neglecting ring conformations, it is easily seen that the *cis-α* and *cis-β* isomers exist as enantiomeric pairs, and these five isomers have been observed for the ion Co(trien)Cl_2^+. In these complexes the secondary nitrogen atoms become optically active upon coordination with their particular configuration being determined by the conformations of the attached chelate arms.

There have been no quantitative studies of isomer distribution as a function of the steric interaction between conformations of the two arms and backbone in these tetramine ligands. However, qualitative studies using molecular models indicate that the stability of an isomer is dependent upon the conformations of the various ring systems. Experimental results support the predictions made for complexes of the ligand LL-α,α'-$(CH_3)_2$trien,[4a,b] where the arms are expected to prefer the k conformation,[10] but only three of the five possible isomers were isolated.[10] They were: D-*cis-α*, 95%; L-*cis-β*, 4%; optically active *trans*, 1% of the yield.

Also, the ligands



$$(NH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HNHCH_2\text{-})_2$$



LL-β,β'-$(CH_3)_2$trien[4c] and D-N,N-2-picolyl-1-methyl-1,2-diaminoethane,[4d] respectively, have been shown to coordinate stereoselectively. Although Yoshikawa, Sekihara, and Goto[4c] did isolate only an optically active *trans* complex which thus showed the stereoselective nature of their ligand, their preparative work suggests that other isomers might be isolable if the mixture were evaporated cold instead of on the steam bath. Bosnich[4d] showed that only the D-*cis-α* isomer was obtained with his ligand which has an optically active carbon of absolute configuration D in the backbone. His analysis indicates that the methyl group is found exclusively in the equatorial position. Thus, it can be concluded that optically active centers in either the arms or backbone of a polyamine ligand will lead to stereoselective coordination. However, it is not possible to predict with certainty what isomers will be isolable because of the presence of kinetic and stereoselective influences in a particular preparative scheme.

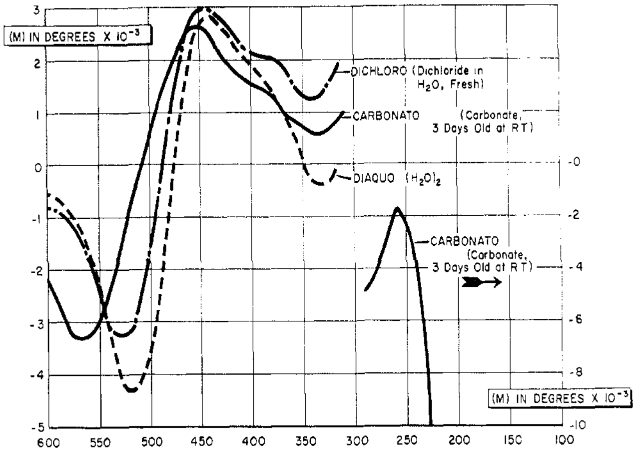


Figure 1.—Optical rotatory dispersion curve for the L-*cis*-β-Co(LDDL)XY^{n+} series.

The polyamines described so far have had only one or two optical centers of the same relative configuration. The new ligand, however, has four optical centers with two different relative configurations in the sequential order L, D, D, and L. This particular ordering of absolute configurations along the polyamine was intended to help limit the isomers formed by the Co(III) coordination complex.

Only two of the five possible isomers were observed, the L-*cis-β* and optically active *trans*. The product distribution was very sensitive to preparative conditions with the *trans* isomer being the only product obtained if the solution was heated above 30° after oxidation and before addition of HCl. It was shown that the L-*cis-β* product isomerized under these conditions to the *trans* product. In fact, this isomerization easily occurred in the solid phase by heating above 110°, by heating the L-*cis-β* product in ethanol for several hours, or by heating an aqueous solution with even a slight excess of hydroxide ion. Thus, these conditions must be rigorously avoided in order to obtain the β product. The ease with which this complex isomerizes to the *trans* configuration is its outstanding feature.

The assignment of absolute configurations for the complexes was made by comparing their ORD spectra with those of the isomers of Co(LL-α,α'-$(CH_3)_2$trien)-Cl_2^+ and Co(trien)Cl_2^+ reported earlier.[10,11] Absorption spectra were not very helpful in making the assign-

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(10) R. G. Asperger, Dissertation, University of Michigan, 1965. Available from University Microfilms, Ann Arbor, Mich. 48104; No. 66-5034.

(11) A. M. Sargeson and G. A. Searle, *Inorg. Chem.*, **4**, 45 (1965). A. M. S. generously supplied samples of the *cis-α* and *cis-β* complexes reported in his paper.

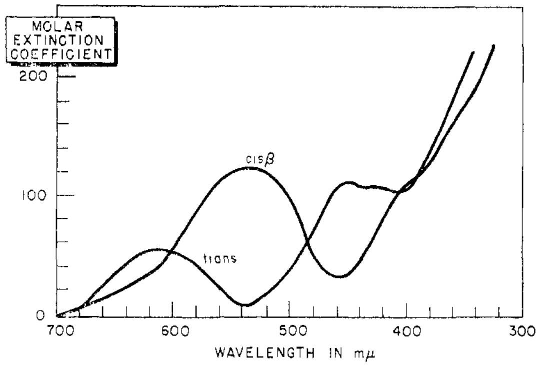


Figure 2.—Absorption spectra of *cis-β*- and *trans*-[Co(LDDL)Cl_2]ClO_4 in methanol as solvent.

ment of the configuration *cis-α* or *cis-β*. The technique used for the complex ions *cis-α*- and *cis-β*-Co(LL-α,α'-$(CH_3)_2$trien)Cl_2^+ is based on the ratio of the extinction coefficient for the high-energy band to that for the low-energy band.[11] However, with the *cis* complex reported here, the onset of the charge-transfer band obscures the higher energy band so that it appears only as a shoulder on the more intense charge-transfer band.

Assignment of *cis* and *trans* isomers can be made using the absorption spectra of the products. These spectra are shown in Figure 2.

A splitting of the lower energy band is expected for the *trans* complex.[12] Figure 2 shows a symmetrical lower energy band for the *trans* complex. However, there are two components to the higher energy band. It is possible that the lower energy component of this higher energy band is really split out of the lower energy band. This interpretation supports the assignment of the *trans* configuration to the green product. The absorption spectrum[13] of *trans*-$(-)_{546}$[Co((−)pn)$_2Cl_2$]Cl in methanol is nearly identical with the spectra of our *trans* complexes.

The only *cis* isomer obtained[10,11] formed crystals of a color more like that of other *cis-β* than like that of *cis-α* complexes. Also, if the complex were *cis-α*, conversion to the *trans* configuration would most likely occur by initial conversion to a *cis-β* configuration. In neither the base-catalyzed isomerization nor the thermal isomerization was there any evidence for a second *cis* isomer. The conversion from *cis-α* to *trans* is represented in Scheme I. Thus, chemical evidence also supports the *β* structural assignment.

The ORD of the isolated isomer shows a negative Cotton effect in the first absorption band and is thus assigned the L absolute configuration. The assignment of the *β* structure is supported by the fact that the ORD spectra of the diaquo, dichloro, and carbonato derivatives of this isomer are related to each other in the same way as are the spectra of the analogous derivatives[10] of the L-*cis-β*-Co(LL-α,α'-$(CH_3)_2$trien)Cl_2.$^+$ The analogous derivatives of D-*cis-α*-Co(LL-α,α'-$(CH_3)_2$trien)Cl_2^+ have quite different relationships.[10] Thus, the *cis* complex obtained is assigned the absolute configuration L-*cis-β*.

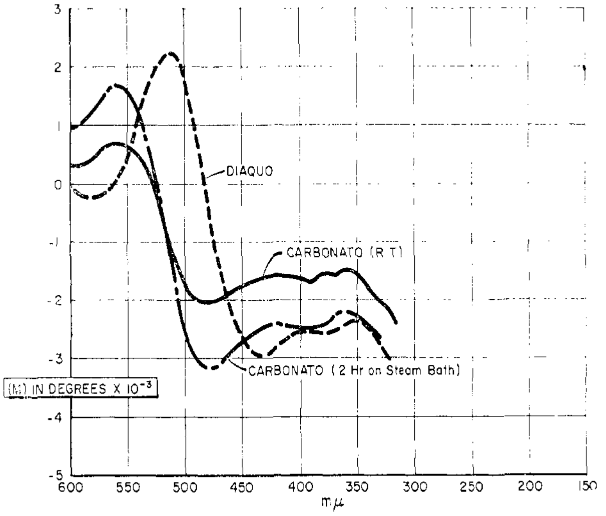
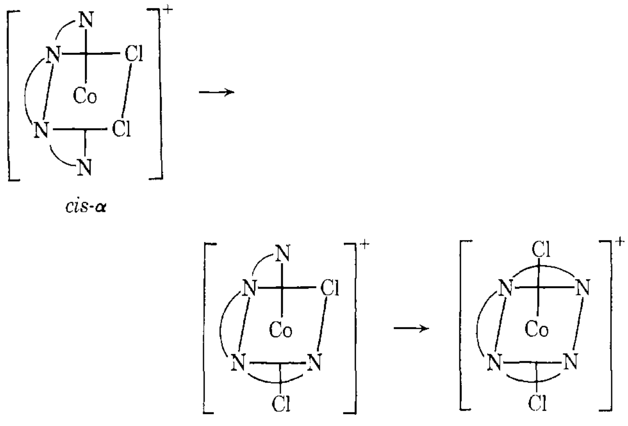


Figure 3.—Optical rotatory dispersion for the *trans*-Co(LDDL)XY^{n+} series.

Scheme I

Isomerization Route for the *cis-α* Isomer Converting to the *trans* Isomer



The ORD spectra of the *trans* complexes prepared are shown in Figure 3. The green isomer was dissolved in water and excess carbonate ion was added to yield, *in situ*, the product called carbonato (R.T.) after standing at room temperature for 2 hr. If this product was heated on the steam bath for 2 hr, the product called carbonato (2 hr on steam bath) was observed *in situ*. The two products have identical Cotton effects with only peak heights and troughs being of different magnitude but occurring at identical wavelengths. This indicates a probable conformational conversion. All of these isomers gave unintelligible proton nmr spectra due to the large number of overlapping absorptions, thereby eliminating this technique for the documentation of the proposed conformational conversion. Addition of perchloric acid yielded the diaquo species which, on evaporation to dryness after adding HCl, yielded a green product which had an ir

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(12) R. G. Wilkins and J. G. Williams in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 190.

(13) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc., A*, 1304 (1968) (their Figure 3).

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

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

Acknowledgments.—The author wishes to express his appreciation to Drs. W. B. Neely and P. J. Oriel of The Biochemicals Research Laboratories, The Dow Chemical Co., for their stimulating discussions.

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

BY M. DALE ALEXANDER AND HOBART G. HAMILTON, JR.

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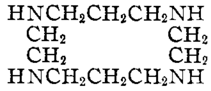
Cobalt(III) complexes of the new tetramine ligand, 4,7-diaza-1,10-decanediamine, $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$ (3,2,3-tet), have been prepared and characterized. One of these, *trans*-$Co(3,2,3\text{-tet})Cl_2^+$, aquates in acidic solution with retention of topology to yield *trans*-$Co(3,2,3\text{-tet})(H_2O)Cl^{2+}$: $\Delta H^{\ddagger} = 24.5$ 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),



$$\begin{array}{lcr} \mathrm{HNCH_2CH_2CH_2NH} & & \\ \mathrm{CH_2} & & \mathrm{CH_2} \\ \mathrm{CH_2} & & \mathrm{CH_2} \\ \mathrm{HNCH_2CH_2CH_2NH} & & \end{array}$$

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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