vents. Both imidazole and porphyrins are known to form aggregates of a donor–acceptor type in solution[15,16] and so the reason for the dependence of β_{21} on imidazole may be the interaction of FeTPPIm$_2$Cl with additional imidazole. This and other possibilities are currently under consideration in our laboratory. In any event, the effect has a striking consequence in benzene. At 8.0×10^{-5} M in FeTPPCl, the imidazole concentration may be varied from 0.5×10^{-3} to 3×10^{-3} M to give spectra with isosbestic points and complete formation of the bis-imidazole complex. Solutions about 1.5×10^{-3} M in imidazole deposit lustrous blue crystals over several days time to become nearly clear. The crystals are the bis-imidazole complex and they may be redissolved by raising the imidazole concentration of the mother liquor to about 3.0×10^{-3} M, indicating the strong solvating effect of higher concentrations of the heterocycle.

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The last point of discussion is the complete absence of any detectable polymerization of FeTPPCl in any of the solvents studied. All work was carried out at several concentrations of FeTPPCl and no dependence of β_{21} on FeTPPCl could be observed. Polymerization of this porphine evidently is not a problem, possibly because of the steric requirements of the phenyl groups, which are tilted about 80° out of the porphine plane.[3-5]

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Conformational Studies of Metal Chelates. II. Stereochemistry and Conformational Analysis of the Cobalt(III) Complexes of 4,7-Diaza-5(R)-methyl-1,10-decanediamine

LOUIS J. DeHAYES and DARYLE H. BUSCH*

The optically active ligand 4,7-diaza-5(R)-methyl-1,10-decanediamine (3.2′.3.) was prepared from previously resolved (R)-1,2-propanediamine. The cobalt(III) complexes *trans*-[Co(R-3.2′.3.)Cl$_2$]$^+$ and *cis*-[Co(R-3.2′.3.)ox]$^+$ were prepared and characterized. The methods of semiempirical conformational analysis were applied to the possible isomers of these complexes to support the structural assignments. Both conformational enthalpies and entropies were calculated using the minimization scheme of Boyd. From among the six possible trans conformers, the calculations show that the complex having the structure *trans*-(SS)-[Co(R-3.2′.3.)$\gamma\lambda\gamma$Cl$_2$]$^+$ is greatly favored and this structure has been assigned to the trans isomer isolated. This isomer can be converted into a cis isomer that must be either Λ-β-cis-(SS)-[Co(R-3.2′.3.)ox]$^+$ or Δ-α-cis-(SS)-[Co(R-3.2′.3)ox]$^{2+}$ if the reaction is conducted in acidic media without inversion of secondary nitrogen atoms. Based on the circular dichroism spectrum of the cis compound, it has the Λ chirality; it is Λ-β-cis-SS. The results of the conformational calculations support this assignment, indicating that the α-cis isomer is less stable by almost 3 kcal/mol.

Introduction

Transition metal complexes[1] of linear tetradentate ligands provide an interesting and fruitful area for observing and studying the subtle interrelations of structure, stereochemistry, and stereospecificity. Since the early work of Sargeson and coworkers[2] with triethylenetetramine, investigations have expanded in a number of directions: (a) the synthesis of linear tetradentate ligands with other donor atoms besides nitrogen (*e.g.*, N$_2$S$_2$, N$_2$O$_2$, S$_4$, As$_2$S$_2$, P$_2$S$_2$);[3-5] (b) the synthesis of optically active methyl-substituted triethylene-tetramines;[6-9] (c) the synthesis of tetramines with different sizes of chelate rings.[10,11]

Assignment of detailed structures to conformational isomers in these systems has been achieved with difficulty, and in some cases ambiguities remain. One of the most promising tools for the assignment of conformational isomers in transition metal complexes is modern conformational analysis. The availability of large computers and efficient minimization schemes has made these semiempirical calculations feasible for systems with a large number of atoms. Calculations of the relative strain energies for different conformers

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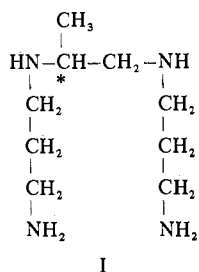(10) M. D. Alexander and H. G. Hamilton, *Inorg. Chem.*, 5, 2060 (1966); 8, 2131 (1969).
(11) J. G. Gibson and E. D. McKenzie, *J. Chem. Soc. A*, 1092 (1971).

of transition metal chelates have recently appeared in the literature[12] and we report here the application of these calculational techniques to complexes of the linear tetradentate ligand $NH_2CH_2CH_2CH_2NHCH_2CH(CH_3)NHCH_2CH_2CH_2NH_2$ (abbreviated 3.2'.3.).

Two observations have strongly influenced our studies with this class of ligand. Studies on the methyl-substituted triethylenetetramines have shown that methyl substitution can be used in determining absolute configurations, while the studies on tetramines with six-membered chelate rings (2.3.2. and 3.2.3.) have shown a notable tendency for these ligands to stabilize the *trans*-diacidotetramine geometry.[10] Our intent has been to compare the results of the calculations on a system incorporating these two features with the appropriate synthetic results, with the threefold aim of deducing the detailed conformation of the trans isomer, determining the absolute configuration of the complex, and rationalizing the observed preference for the trans geometry.

The ligand synthesized for our studies was 4,7-diaza-5(*R*)-methyl-1,10-decanediamine [5(*R*)-3.2'.3.] (structure I). Upon complexation, this ligand forms a five-membered chelate ring flanked by two six-membered chelate rings and contains a methyl substituent on a carbon atom of known absolute configuration within the five-membered chelate ring. Thus, we might expect the ligand to yield predominantly one *trans*-diacido isomer whose conformation will be determined by the absolute configuration of the carbon atom bearing the methyl substituent. This expected isomer is *trans*-(*SS*)-[Co[5(*R*)-3.2'.3.] $\gamma\lambda\gamma Cl_2$]$^+$ where "*SS*" refers to the configurations[13] of the coordinated secondary nitrogens and the $\gamma\lambda\gamma$ describes the chelate ring conformations. [γ = a (six-membered) chair conformation, λ a (five-membered) gauche ring.][14] This isomer is depicted in Figure 1.

An additional feature of this system is that the assignment of the structure of the trans isomer provides a useful new comparison between an experimental circular dichroism spectrum and that predicted by sector rules that have been proposed for correlating circular dichroism effects with the configurations of pseudo-tetragonal complexes.

$$CH_3$$
$$|$$
$$HN-CH-CH_2-NH$$
$$|\quad * \qquad\qquad |$$
$$CH_2 \qquad\qquad CH_2$$
$$|\qquad\qquad\qquad |$$
$$CH_2 \qquad\qquad CH_2$$
$$|\qquad\qquad\qquad |$$
$$CH_2 \qquad\qquad CH_2$$
$$|\qquad\qquad\qquad |$$
$$NH_2 \qquad\qquad NH_2$$

I

Experimental Section

Physical Measurements. Electronic absorption spectra were recorded on a Cary Model 14-R recording spectrophotometer using matched 1-cm quartz cells. Circular dichroism spectra were recorded on a Jasco ORD/UV-5 which has been fitted with a Sproul Scientific SS-20 CD modification. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Computer Calculations. All computer calculations were performed at the Instructional and Research Computer Center of the Ohio State University utilizing their IBM System 360/50, 360/75, or
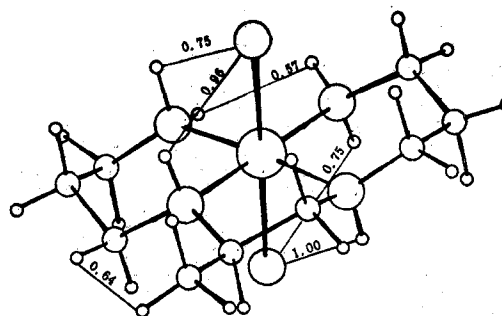
Figure 1. The *trans*-(*SS*)-[Co(*R*-3.2'.3.)$\gamma\lambda\gamma Cl_2$]$^+$ complex; nonbonded interactions >0.50 kcal/mol.

370/165 computers. The programs used are as described earlier.[15,16]

(*R*)-**6-Methyl-1,5,8,12-tetraazadodecane.** This synthesis is based on the work of Israel, Rosenfield, and Modest.[17] (*R*)-1,2-Propanediamine was resolved by the method of Dwyer,[18] distilled, and dried over sodium metal. This pure, *dry* diamine (6.33 g, 0.0854 mol) was placed in a three-necked round-bottomed flask in an ice bath. The flask was then fitted with a condenser and dropping funnel. Freshly distilled acrylonitrile (9.04 g, 0.1708 mol) was added dropwise and the flask was maintained under a dry nitrogen flow. After the addition of acrylonitrile was completed, the reaction mixture was allowed to warm to room temperature. It was brought slowly to 80° and maintained at this temperature for several hours. The reaction mixture was then distilled under vacuum (1-2 mm) until the pot temperature rose to 100° to remove unreacted acrylonitrile, diamine, and monocyanoethylated diamine. The remainder of the reaction mixture was assumed to be the desired dicyanoethylated diamine, which was then dissolved in absolute ethanol (300 ml) and saturated with dry ammonia at 0°. About 5 g of Raney Nickel No. 28 catalyst was added to the solution and the slurry was then placed on a Parr hydrogenator at 55-65 psi for 24-36 hr at room temperature. After the hydrogenation was complete (absence of C=N in ir) the catalyst was carefully removed by filtration and the ethanol was removed on a rotary evaporator. The remaining oil was then vacuum distilled. The desired tetramine has a bp of 130° at 1-2 mm of pressure. Purity was checked by gas chromatography and nmr, both of which showed that there was no triamine present.

trans-(*SS*)-[Co(*R*-3.2'.3.)Cl$_2$]Cl·2H$_2$O·HCl. Cobalt chloride hexahydrate (1.19 g, 0.005 mol) was dissolved in 20 ml of methanol containing 0.5 ml of concentrated HCl. A methanol solution of the ligand (0.005 mol) was added to the cobalt solution and the mixture was refluxed for 30 min. The condenser was removed and air was bubbled through the solution for an additional 15 min. The solution was filtered and the filtrate evaporated to yield a green solid. This solid was dissolved in 0.5 *N* HCl and placed on a Dowex 50 W-X4 column and eluted with 0.5 *N* HCl. The sample gave only one band. Green crystals gradually formed in the eluent. *Anal.* Calcd for [Co(L)Cl$_2$]Cl·2H$_2$O·HCl: C, 25.37; H, 6.86; N, 13.15; Cl, 33.28. Found: C, 25.40; H, 7.06; N, 13.30; Cl, 33.20.

trans-[Co(*R*-3.2'.3.)Cl$_2$]ClO$_4$. A sample of the chloride salt was dissolved in H$_2$O and several drops of a saturated solution of NaClO$_4$ were added. A light green powder precipitated. This powder was air-dried and then dissolved in hot CH$_3$CN. Upon cooling, fine green needles formed. *Anal.* Calcd for [Co(*R*-3.2'.3.)Cl$_2$]ClO$_4$: C, 25.86; H, 5.79; N, 13.41. Found: C, 26.07; H, 5.93; N, 13.53.

cis-[Co(*R*-3.2'.3.)ox]ClO$_4$. The trans complex (0.005 mol) as the perchlorate salt was dissolved in a solution containing 0.005 mol of oxalic acid and warmed for several hours on a steam bath. The solution turned red violet, and after cooling and concentrating the solution, red-violet crystals formed. These were dissolved in H$_2$O and passed over a Dowex 50 W-X4 ion-exchange column and eluted with 0.1 *N* NaClO$_4$ solution. A small sample was also tested on tlc and both trials showed evidence of only one isomer. *Anal.* Calcd for [Co(*R*-3.2'.3.)ox]ClO$_4$: C, 30.41; H, 5.52; N, 12.89; Cl, 8.16; O, 29.46. Found: C, 30.38; H, 5.60; N, 12.81; Cl, 8.10; O, 29.56.

Conformational Analysis. Calculations of the conformational energies of the possible isomers in this system were undertaken using

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the classical model of the strained molecule.[19-22] The results of the calculations represent an estimate of the structural deformation or instability of a given system. The conformational or strain energy is defined as

$$U = U_R + U_\theta + U_\phi + U_{NB}$$

where U_R is the energy associated with bond stretching, U_θ is the energy resulting from bond angle deformation, U_ϕ is the energy involving bond torsions, and U_{NB} arises from the nonbonded or van der Waals interactions in the molecule.

Using this approach, the difference in the calculated conformational energies of two molecules, or isomers, approximates a relative conformational enthalpy difference. This enthalpy, in turn, can be related to a "conformational free energy" upon consideration of an appropriate entropy contribution.

The potential functions, force constants, and calculational scheme are all identical with that described earlier.[15] Minimization of the strain energy was accomplished utilizing the modified Newton-Raphson method of Boyd.[16] One advantage of this approach to minimization is that the same matrix used in the minimization can be used to calculate a set of vibrational energy levels for the molecule.[16,23,24] These $(3N - 6)$ vibrational energy levels can in turn be used to evaluate the vibrational contribution to the entropy. The classical entropy contribution to the free energy of the system is then obtained by summing this vibrational entropy with the readily calculated translational, rotational, and statistical entropies. This final entropy term can then be combined with our conformational enthalpy (strain energy) to yield a relative conformational free energy for the molecule or conformer.

$$G = (U_R + U_\theta + U_\phi + U_{NB}) - TS$$

Results and Discussion

The optically active linear tetradentate ligand, 5(R)-Me-3.2'.3. was prepared and its complexes with cobalt(III) were prepared. A green dichloro complex was isolated and, on the basis of its visible spectrum,[25] assigned the trans (D_{4h}) geometry. In addition, a violet oxalato complex was isolated and assigned the β-cis configuration.

The CD spectrum of the trans isomer has been recorded and reported earlier.[25] On the basis of the correlations between the chelate ring conformations, the secondary amine configurations, and the signs of the A_2 and E_a bands in the CD spectrum, which we proposed earlier,[25] the trans complex was assigned the absolute configuration depicted in Figure 1 which is analogous to that of the 3.2.3. complex whose structure has since been determined.[26] In order to confirm this assignment for the 3.2'.3. ligand and to rationalize the stability of the *trans*-diacido complexes *vs.* that of cis-β and cis-α complexes, we undertook a detailed conformational analysis of this system.

Figures 1-6 contain representations of six possible trans conformers while Figures 7 and 8 depict two β-cis complexes and Figure 9, an α-cis structure. Among the trans conformers we have examined, the principal sources of strain (relative to the *trans*-(SS)-[Co(R-3.2'.3.)$\gamma\lambda\gamma$Cl$_2$]$^+$ conformer) can be traced to three effects: (1) the axial methyl group, (2) ring strain due to the conformation of the central chelate ring, and (3) the relative orientation of the two γ six-membered chelate rings. These sources of strain are summarized in Table I for the six trans conformers. If we examine the structures for the two trans conformers with axial methyl

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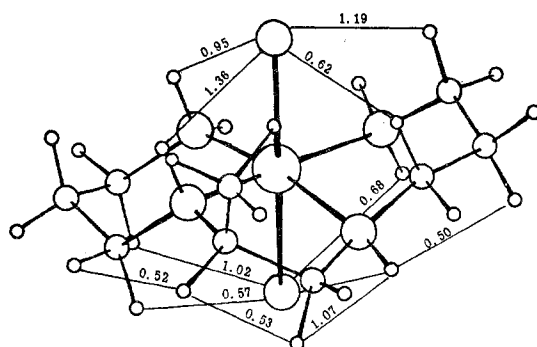(26) N. C. Payne, *Inorg. Chem.,* **12,** 1151 (1973).

Figure 2. The *trans-(SS)*-[Co(R-3.2'.3.)$\gamma\delta\gamma$Cl$_2$]$^+$ complex; nonbonded interactions >0.50 kcal/mol.
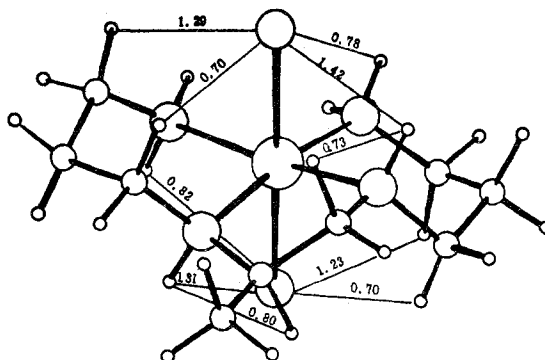

Figure 3. The *trans-(RR)*-[Co(R-3.2'.3.)$\gamma\lambda\gamma$Cl$_2$]$^+$ complex; nonbonded interactions >0.50 kcal/mol.
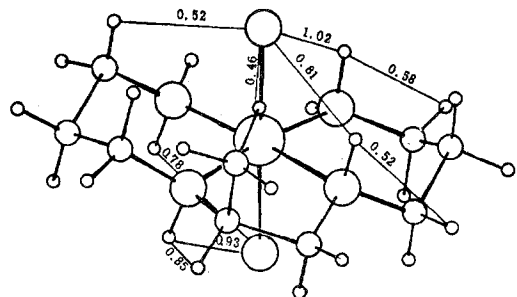
Figure 4. The *trans-(RR)*-[Co(R-3.2'.3.)$\gamma\delta\gamma$Cl$_2$]$^+$ complex; nonbonded interactions >0.50 kcal/mol.
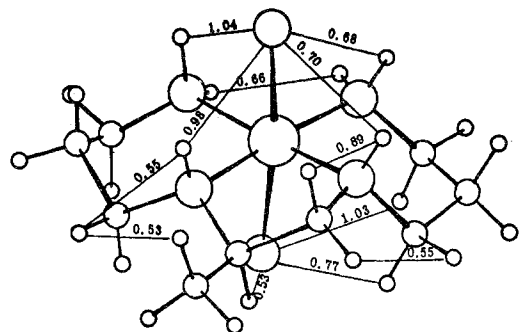
Figure 5. The *trans-(SR)*-[Co(R-3.2'.3.)$\gamma\lambda\gamma$Cl$_2$]$^+$ complex; nonbonded interactions >0.50 kcal/mol.

substituents (Figure 2 and 4), we note that there are no severe (>0.50 kcal/mol) interactions between the axial methyl and the axial Cl$^-$ ligand. The reason for this can be seen in the torsional angles for these complexes which are listed in Table II. We can see from the C-N and N-Co torsional angles that the five-membered chelate rings are severly flattened. This flattening of the rings causes the methyl group to move away from the adjacent chloride ligand. This ring flattening affects both the θ and ϕ terms for these two conformers.

Figure 6. The *trans-(RS)*-[Co(*R*-3.2'.3.)γλγCl$_2$]$^+$ complex; nonbonded interactions >0.50 kcal/mol.
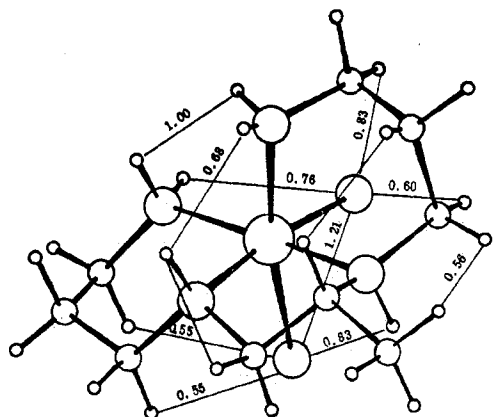
Figure 7. The Λ-β$_1$-*cis*-[Co(*R*-3.2'.3.)γλγCl$_2$]$^+$ complex; nonbonded interactions >0.50 kcal/mol.
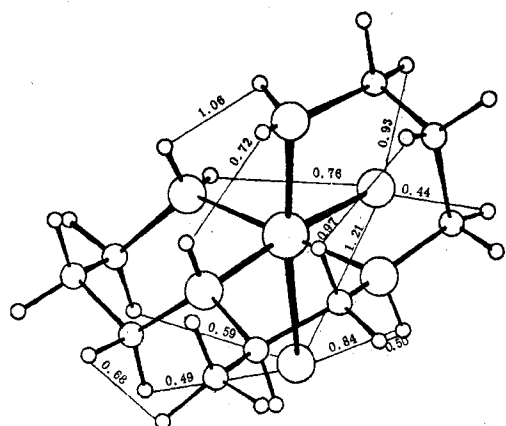
Figure 8. The Λ-β$_2$-*cis*-[Co(*R*-3.2'.3.)γλγCl$_2$]$^+$ complex; nonbonded interactions >0.50 kcal/mol.

Figure 9. The Δ-α-*cis*-[Co(*R*-3.2'.3.)γλγCl$_2$]$^+$ complex; nonbonded interactions >0.50 kcal/mol.

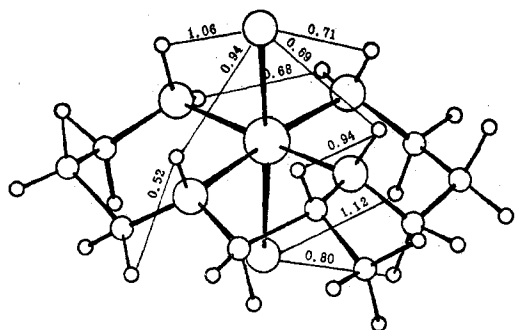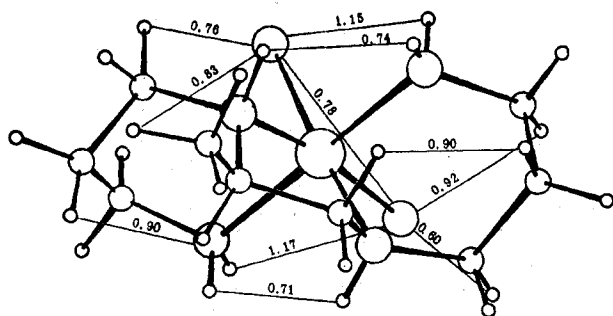The ring strain results from the fact that for a given configuration of the secondary nitrogens, *SS* or *RR*, there is a corresponding preferred conformation for the central chelate ring.

If the nitrogens are *SS* then the five-membered ring "prefers" the λ conformation; conversely, if the nitrogens are *RR* the ring "prefers" the δ conformation. For a separate ethylenediamine ligand, when one flips the conformation of the unsubstituted chelate ring from λ to δ or from δ to λ, the NH's exchange relative positions, the axial NH's become the equatorial NH's while the equatorial NH's become the axial NH's. In a fused system, as in the linear tetradentates, there is one N–H bond per secondary amine, the other bond being an N–C bond in the adjacent ring. If one attempts to flip the conformation of the center chelate from its "preferred" conformation, then the nitrogen attempts to exchange the relative positions of the N–H and N–C bonds. In order for this to occur the N–C bond would have to increase in length by ~0.3 Å. This cannot realistically happen and what we observe is a severe flattening of the ring and a marked increase in strain in the angles about the secondary nitrogens. By comparing Tables I and III we can see that for all the trans conformers in which the central chelate ring is in an unfavorable conformation, the θ strain energies are notably higher than in the other cases. A large portion of this θ strain energy can be attributed to the C–N–C angles. The values for these angles are given in Table IV. We can also see in Table II that the torsions about the C–C bonds in the central chelate rings in these complexes are also lower than for those cases in which the ring is in a preferred conformation. The third difference in the strain for the series of trans conformers arises from the relative orientation of the two six-membered rings. As shown in Table I these rings can be "cis" or "trans" to each other with respect to the CoN$_4$ plane. By examining the nonbonded repulsions for the two conformers with these rings "cis" and comparing them to the most stable trans conformer where the rings are "trans" we can see significant increases in the nonbonded repulsions between the axial ligands and the axial N–H's and axial C–H's on the six-membered chelate rings. In addition to these nonbonded repulsions, the "cis" arrangement of γ rings requires the secondary amines to have opposite configurations, *RS* or *SR*. As a consequence of this there is no preferred conformation for the central chelate ring itself, and its conformation, δ or λ, is determined by the configuration of the methyl substituent. This shows up in the geometry both in the Co–N torsional angles for the central chelate ring which are severely distorted relative to the most stable *trans-(SS)*-[Co-(*R*-3.2'.3.)γλγCl$_2$]$^+$ conformer and in the φ term in Table III. For these reasons the *trans-(SS)*-[Co(*R*-3.2'.3.)γλγCl$_2$]$^+$ conformer, with a "trans" arrangement of γ rings, an equatorial methyl group, and no "ring strain," is predicted to be the most stable. This has been confirmed by the results of crystallographic studies on *trans*-[Co(3.2.3.)Cl$_2$]$^+$ [26] and (+)$_{546}$-*trans*-[Co(3.2.3.)(NO$_2$)$_2$]$^+$.[27]

Examination of Table III also shows that this trans conformer is considerably more stable than either the β-cis or α-cis isomers. The reason for this can be seen in the nonbonded (NB) term in Table III as well as in the figures, where we can see in the cis isomers interactions between the central methylene of the γ ring and the axial C–H on the central chelate ring of almost 1 kcal/mol. We also see additional interactions between the N–H's in the cis isomers which are not present for the trans isomer. In Table II we can see that there are also small increases for the C–C–C and C–C–N angles in the cis isomers. Based on these observations we might have expected the β-cis isomers to be more stable than the α-cis simply because they have only half as many of these

(27) N. C. Payne, *Inorg. Chem.*, **11**, 1376 (1972).

Table I. Sources of Strain for the *trans*-[Co(R-3.2'.3.)Cl₂]⁺ Conformers

Conformer	Methyl group	Ring strain	Six-membered rings
trans-(SS)-[Co(R-3.2'.3.)γλγCl₂]⁺	Equatorial	No	Trans
trans-(SS)-[Co(R-3.2'.3.)γδγCl₂]⁺	Axial	Yes	Trans
trans-(RR)-[Co(R-3.2'.3.)γλγCl₂]⁺	Equatorial	Yes	Trans
trans-(RR)-[Co(R-3.2'.3.)γδγCl₂]⁺	Axial	No	Trans
trans-(SR)-[Co(R-3.2'.3.)γλγCl₂]⁺	Equatorial	No	Cis
trans-(RS)-[Co(R-3.2'.3.)γλγCl₂]⁺	Equatorial	Yes	Cis

Table II

Minimized Bond Lengths for the [Co(R-3.2'.3.)Cl₂]⁺ Isomers

Conformer	Co-N	N-C	C-C	C-C	C-N	C-N	N-Co	N-Co	C-N	C-N	C-C	C-C	N-C	N-C	N-Co
trans-(SS)-[Co(R-3.2'.3.)γλγCl₂]⁺	2.06	1.49	1.55	1.55	1.49	1.49	2.06	2.06	1.49	1.49	1.55	1.55	1.49	1.49	2.06
trans-(SS)-[Co(R-3.2'.3.)γδγCl₂]⁺	2.06	1.49	1.56	1.55	1.50	1.49	2.06	2.06	1.49	1.49	1.55	1.55	1.49	1.49	2.06
trans-(RR)-[Co(R-3.2'.3.)γλγCl₂]⁺	2.06	1.50	1.56	1.55	1.50	1.50	2.05	2.05	1.49	1.50	1.56	1.55	1.49	1.49	2.05
trans-(RR)-[Co(R-3.2'.3.)γδγCl₂]⁺	2.06	1.50	1.56	1.55	1.50	1.50	2.03	2.03	1.49	1.50	1.56	1.55	1.49	1.50	2.06
trans-(SR)-[Co(R-3.2'.3.)γλγCl₂]⁺	2.06	1.49	1.56	1.55	1.49	1.49	2.05	2.05	1.49	1.49	1.55	1.55	1.49	1.49	2.05
trans-(RS)-[Co(R-3.2'.3.)γλγCl₂]⁺	2.06	1.49	1.56	1.55	1.50	1.50	2.06	2.06	1.49	1.50	1.55	1.55	1.49	1.49	2.04
Λ-β₁-*cis*-(SS)-[Co(R-3.2'.3.)Cl₂]⁺	2.07	1.49	1.55	1.55	1.49	1.48	2.06	2.06	1.49	1.48	1.55	1.55	1.49	1.49	2.05
Λ-β₂-*cis*-(SS)-[Co(R-3.2'.3.)Cl₂]⁺	2.07	1.49	1.55	1.55	1.50	1.49	2.05	2.05	1.49	1.49	1.55	1.55	1.50	1.49	2.07
Δ-α-*cis*-(SS)-[Co(R-2.3'.3.)Cl₂]⁺	2.07	1.49	1.55	1.55	1.50	1.49	2.05	2.05	1.49	1.50	1.55	1.55	1.50	1.49	2.06

Minimized Bond Angles for the [Co(R-3.2'.3.)Cl₂]⁺ Isomers

Conformer	N-Co-N	Co-N-C	N-C-C	C-C-C	C-C-N	C-N-Co	C-N-Co	N-Co-N	Co-N-C	N-C-C	C-C-C	C-C-N	N-C-C	C-N-Co
trans-(SS)-[Co(R-3.2'.3.)γλγCl₂]⁺	91.14	120.88	112.08	111.10	111.73	119.91	106.08	86.33	106.11	108.83	107.52	111.77	112.14	120.36
trans-(SS)-[Co(R-3.2'.3.)γδγCl₂]⁺	94.08	120.37	111.90	111.12	111.91	119.26	110.64	84.81	106.84	109.99	107.44	112.22	112.15	120.53
trans-(RR)-[Co(R-3.2'.3.)γλγCl₂]⁺	87.75	119.55	113.57	113.61	110.85	115.44	105.06	88.09	105.70	109.50	109.46	113.29	111.24	119.16
trans-(RR)-[Co(R-3.2'.3.)γδγCl₂]⁺	86.86	119.91	113.66	113.31	110.97	116.79	109.78	87.10	107.64	112.59	110.19	112.80	112.04	119.41
trans-(SR)-[Co(R-3.2'.3.)γλγCl₂]⁺	85.97	118.87	112.51	113.26	110.92	116.56	104.74	86.17	107.67	109.86	107.29	111.97	111.82	119.76
trans-(RS)-[Co(R-3.2'.3.)γλγCl₂]⁺	86.78	118.57	112.37	113.92	112.22	115.43	104.68	86.68	106.67	109.16	108.09	112.35	111.38	120.44
Λ-β₁-*cis*-(SS)-[Co(R-3.2'.3.)Cl₂]⁺	86.31	120.96	112.95	112.00	114.72	118.30	106.02	86.22	106.73	107.80	108.87	111.53	112.61	120.42
Λ-β₂-*cis*-(SS)-[Co(R-3.2'.3.)Cl₂]⁺	86.69	120.84	112.76	112.36	114.96	120.45	105.86	86.38	106.66	109.30	107.67	111.29	113.03	120.00
Δ-α-*cis*-(SS)-[Co(R-2.3'.3.)Cl₂]⁺	85.69	119.86	112.54	112.62	115.01	120.40	106.97	86.04	106.96	109.16	107.89	112.71	114.79	119.98

Conformer	N-Co-N	Co-N-C	N-C-C	C-C-C	C-C-N
trans-(SS)-[Co(R-3.2'.3.)γλγCl₂]⁺	92.85	118.50	72.46	70.26	54.10
trans-(SS)-[Co(R-3.2'.3.)γδγCl₂]⁺	90.56	118.99	69.73	67.34	56.63
trans-(RR)-[Co(R-3.2'.3.)γλγCl₂]⁺	89.20	114.60	66.33	58.80	55.71
trans-(RR)-[Co(R-3.2'.3.)γδγCl₂]⁺	91.52	115.80	69.29	63.48	54.88
trans-(SR)-[Co(R-3.2'.3.)γλγCl₂]⁺	94.72	118.92	73.60	71.79	50.97
trans-(RS)-[Co(R-3.2'.3.)γλγCl₂]⁺	92.69	120.32	71.96	69.99	52.20
Λ-β₁-*cis*-(SS)-[Co(R-3.2'.3.)Cl₂]⁺	88.05	120.74	66.07	67.05	61.77
Λ-β₂-*cis*-(SS)-[Co(R-3.2'.3.)Cl₂]⁺	90.27	119.37	68.01	68.78	60.09
Δ-α-*cis*-(SS)-[Co(R-2.3'.3.)Cl₂]⁺	85.72	118.31	60.62	59.42	63.30

Minimized Torsional Angles for the [Co(R-3.2'.3.)Cl₂]⁺ Isomers

Conformer	Co-N	N-C	C-C	C-N	N-Co	Co-N	N-C	C-C	C-N	N-Co	Co-N	N-Co	N-Co
trans-(SS)-[Co(R-3.2'.3.)γλγCl₂]⁺	35.04	55.01	68.98	71.05	58.59	36.56	14.59	41.15	56.38	40.95	15.19	34.20	33.45
trans-(SS)-[Co(R-3.2'.3.)γδγCl₂]⁺	28.37	51.05	71.72	73.96	54.36	29.69	20.98	43.58	49.07	29.87	5.60	39.67	38.39
trans-(RR)-[Co(R-3.2'.3.)γλγCl₂]⁺	47.96	56.09	57.81	65.45	70.02	54.17	13.63	38.50	53.64	38.76	14.11	52.49	47.20
trans-(RR)-[Co(R-3.2'.3.)γδγCl₂]⁺	48.37	56.89	57.37	63.88	69.67	54.27	16.03	34.28	39.85	24.66	5.15	45.11	41.65
trans-(SR)-[Co(R-3.2'.3.)γλγCl₂]⁺	52.62	62.19	59.05	62.46	67.81	54.67	2.93	30.29	53.28	47.55	25.25	29.88	28.69
trans-(RS)-[Co(R-3.2'.3.)γλγCl₂]⁺	52.51	61.74	59.25	53.03	66.91	54.00	4.87	32.02	54.57	47.31	23.75	33.23	31.11
Λ-β₁-*cis*-(SS)-[Co(R-3.2'.3.)Cl₂]⁺	48.33	61.16	59.39	62.08	63.56	47.91	13.48	39.25	55.46	41.74	15.83	21.86	43.27
Λ-β₂-*cis*-(SS)-[Co(R-3.2'.3.)Cl₂]⁺	47.87	62.29	60.04	59.64	59.97	45.81	12.28	38.80	55.25	41.70	16.86	38.55	40.62
Δ-α-*cis*-(SS)-[Co(R-2.3'.3.)Cl₂]⁺	50.55	64.48	59.86	58.04	59.86	47.54	13.82	39.39	53.73	39.55	14.78	49.42	50.81

Table III. Minimized Strain Energies for the $[Co(R\text{-}3.2'.3.)Cl_2]^+$ Complexes[a]

Complex	R	NB	θ	ϕ	ΔH	$T\Delta S$	ΔG
trans-(SS)-$[Co(R\text{-}3.2'.3.)\gamma\lambda\gamma Cl_2]^+$	2.33	1.79	6.02	1.09	0.00	0.00	0.00
trans-(SS)-$[Co(R\text{-}3.2'.3.)\gamma\delta\gamma Cl_2]^+$	2.58	5.78	9.29	2.94	9.37	-0.57	9.94
trans-(RR)-$[Co(R\text{-}3.2'.3.)\gamma\lambda\gamma Cl_2]^+$	2.45	4.88	10.27	1.43	7.79	-0.65	8.44
trans-(RR)-$[Co(R\text{-}3.2'.3.)\gamma\delta\gamma Cl_2]^+$	2.49	2.81	7.00	1.70	2.78	-0.69	3.47
trans-(SR)-$[Co(R\text{-}3.2'.3.)\gamma\lambda\gamma Cl_2]^+$	2.46	3.42	7.03	1.80	3.47	-0.29	3.76
trans-(RS)-$[Co(R\text{-}3.2'.3)\gamma\lambda\gamma Cl_2]^+$	2.61	3.79	7.94	1.31	4.43	-0.50	4.93
$\Lambda\text{-}\beta_1\text{-}cis$-(SS)-$[Co(R\text{-}3.2'.3.)Cl_2]^+$	2.76	3.31	7.84	0.59	3.28	-0.29	3.57
$\Lambda\text{-}\beta_2\text{-}cis$-(SS)-$[Co(R\text{-}3.2'.3)Cl_2]^+$	2.79	3.66	7.70	0.76	3.68	-0.17	3.85
$\Delta\text{-}\alpha\text{-}cis$-(SS)-$[Co(R\text{-}3.2'.3.)Cl_2]^+$	3.11	4.42	8.82	0.69	5.81	-0.73	6.54

[a] $T = 298.15°$K.

Table IV. Comparison of Conformers with and without "Ring Strain"

Conformer	C–N–C	$(\theta,$ kcal/mol)	C–N–C	$(\theta,$ kcal/mol)
trans-(SS)-$[Co(R\text{-}3.2'.3.)\gamma\lambda\gamma Cl_2]^+$	110.6°	(0.02)	112.5°	(0.13)
trans-(SS)-$[Co(R\text{-}3.2'.3.)\gamma\delta\gamma Cl_2]^+$	116.2°	(0.69)	113.5°	(0.25)
trans-(RR)-$[Co(R\text{-}3.2'.3.)\gamma\lambda\gamma Cl_2]^+$	115.0°	(0.47)	117.4°	(0.95)

inter-ring interactions, and Table III confirms this conclusion. There are two possible β-cis isomers with the same absolute configurations and secondary amine configurations. These two isomers differ only in the position of the methyl group. For the β_1-cis isomer the methyl group is adjacent to the out-of-plane chelate ring while for the β_2-cis isomer the methyl lies in the CoN_4 plane. The calculations predict the β_1-cis isomer to be the more stable by 0.28 kcal/mol. This difference can be attributed mainly to the methyl-CH(γ) repulsion and the CH_{eq}–NH_{ax} interaction in the five-membered chelate ring. These two interactions are lower in the β_1-cis isomer by 0.25 kcal/mol. From the configuration of the trans complex it is possible to show experimentally that, in accord with the calculations, the cis isomer is of the β-cis geometry. If we assume that the secondary amines do not invert in an acidic medium, there are only two possible configurations for a cis isomer derived from the most stable *trans-SS* structure.[28]

$$\textit{trans-SS} \xrightarrow[\text{ox}^-]{\text{H}^+} \Lambda\text{-}\beta\text{-cis-}SS \text{ or } \Delta\text{-}\alpha\text{-cis-}SS$$
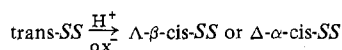
Previously derived correlations[29,30] between absolute configuration and CD spectra permit the assignment of the absolute configuration of the cis isomer. The dominant positive band in the CD (Table V) can be related to the positive E band of the Λ-$[Co(en)_3]$ complex. This leads to the assignment of the Λ absolute configuration for our cis complex. Since the α- and β-cis isomers would have enantiomeric configurations for the same N–H configuration, it follows that the cis-oxalato isomer has the Λ-β-cis-SS configuration.

(28) G. R. Brubaker and D. P. Schaefer, *Inorg. Chem.*, **10**, 968 (1971).
(29) R. E. Ballard, A. J. McCaffery, and S. F. Mason, *Proc. Chem. Soc., London*, 331 (1961).
(30) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

Table V. Visible and CD Data for *cis*-$[Co(\text{tetramine})ox]^+$ Complexes[a]

Complex	λ_{max}	ϵ	λ_{max}	$\Delta\epsilon$	Absolute configuration
(+)-$[Co(en)_2ox]^+$	498	114	521	2.60	Λ
	356	142	385	0.12	
(+)-$[Co(tn)_2ox]^+$	510	79	508	1.21	Λ
	358	147	355	-0.14	
(+)-α-*cis*-$[Co(2.2.2.)ox]^+$	493	110	515	2.95	Λ
	357	123	381	0.57	
			338	0.32	
(+)-β-*cis*-$[Co(2.2.2.)ox]^+$	497	179	515	2.09	Λ
	357	179	388	0.15	
			355	-0.05	
(+)-β-$[Co(2.3.2.)ox]^+$	500	140	535	1.47	Λ
	360	175	475	-0.48	
			370	-0.06	
			340	0.15	
(+)-β-$[Co(3.2.3.)ox]^+$	512	118	555	-0.76	
	363	177	493	1.88	Λ
			353	-0.22	
(+)-β-$[Co(R\text{-}3.2'.3.)ox]^+$	512	120	560	-0.80	
	365	180	495	1.96	Λ

[a] See ref 30.

Other researchers have examined the analogous complexes of the 3.2.3. ligand.[28,31] They, however, originally assigned the complex with a CD spectrum similar to our β-cis complex as the Λ-α-cis-*RR* complex.[28] When they converted their cis complex to a trans isomer, they assigned the trans isomer as a trans-*RR* complex. A comparison of the CD spectra of their trans complex and our trans-*SS* complex showed that the curves are almost superimposable.[25,28,31] This implies that the complexes have the same configurations. Since we know the configuration of the 3.2'.3. complex, the trans complex of 3.2.3. must also have the trans-*SS* nitrogen configurations. The corresponding cis isomer must therefore also be a Λ-β-cis-*SS* complex, as has been pointed out.[31]

(31) J. Cragel and G. R. Brubaker, *Inorg. Chem.*, **11**, 303 (1972).