

Cobalt(III) Complexes with the Disubstituted Tetraamine Ligand 1,10-Diamino-2,9-dimethyl-4,7-diazadecane¹

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As part of our continuing studies of the stereochemistry of transition-metal complexes, cobalt(III) complexes with the tetraamine ligand 1,10-diamino-2,9-dimethyl-4,7-diazadecane were prepared. The two asymmetric carbon centers and two asymmetric nitrogen centers admit the possibility of six unique trans isomers. Two *trans*-dichloro complexes were isolated and characterized by ¹H and ¹³C NMR and by vibrational and electronic spectroscopy. Strain energy minimization calculations indicate the steric requirement for axial methyl substitution exceeds the induced ring strain leading to a high degree of stereoselectivity. Significant distortions in the chelate ring conformations are reflected in increased C-C-C and N-C-C angles of one of the six-membered chelate rings of one isomer. These conformational differences are apparent in both the ¹³C and proton NMR spectra.

Introduction

Cobalt(III) complexes with flexible tetraamine ligands can exist in three topologies (Figure 1²). Of these, the *trans* and *uns-cis* isomers are the most common due, in part, to lower strain energies,³ but the *s-cis* stereochemistry is also known.

The stereocontrol that may be exerted by a single methyl group on the reactions of cobalt(III) complexes is well-known.⁴ The two asymmetric carbon centers of the disubstituted tetraamine ligand along with the two asymmetric nitrogen centers admit the possibility of six different *trans* stereoisomers, only a few of which are expected to be stable. We have undertaken the synthesis of the *trans* complexes in order to explore details of the stereocontrol exerted by the two independent methyl groups of the disubstituted ligand 1,10-diamino-2,9-dimethyl-4,7-diazadecane.

A variety of different instrumental techniques have been used to investigate the stereochemical details of Co(III) complexes. These techniques include electronic spectroscopy,⁵ vibrational spectroscopy,⁵ proton NMR,⁶ carbon-13 NMR,⁷ and X-ray crystallography.⁸ We have found that carbon-13 NMR spectroscopy is extremely sensitive to small changes in the electronic structure of the complex⁹ as well as the steric environment of carbon and is a valuable probe of the stereochemical details of the complex.¹⁰

Experimental Section

Physical Methods. Elemental Analysis. Cobalt analyses were performed with a Varian Model 1200 atomic absorption spectrophotometer. All other analyses (C, H, N) were performed by Guelph Chemical Laboratories, Guelph, Ontario, Canada.

Electronic Spectra. Electronic spectra were measured with a Cary Model 14 spectrophotometer. Solutions were typically 3 × 10⁻³ M in water.

Proton Magnetic Resonance. Proton NMR spectra were measured at 300 MHz with a Nicolet NT-300 NMR spectrometer. Samples

were dissolved in a minimum amount of Me₂SO-*d*₆ (99.9 atom % D, Aldrich). Tetramethylsilane was the internal standard for proton NMR measurements.

Carbon-13 NMR. Carbon-13 NMR spectra were measured with a Varian CFT-20 NMR spectrometer in the deuterium-locked proton noise decoupled mode. Samples were dissolved in Me₂SO-*d*₆ and placed in 10-mm NMR tubes (Wilmad). A pulse width of 21 μs (equivalent to a 90° pulse), a spectral width of 4000 Hz covered by 8192 data points, and an acquisition time of 1.023 s were used for all complexes. Spectra were collected until an acceptable signal to noise ratio was achieved (10000-30000 spectra). All chemical shifts are reported relative to tetramethylsilane, which was the internal standard for this study.

Ion-Exchange Chromatography. A Sephadex C-25 ion-exchange resin in the acid form was used for all ion-exchange experiments.

Molecular Mechanics. Strain energy minimization calculations were performed on a PRIME 400 computer (32 bit internal precision) using a locally modified version of Boyd's MOLBD program.¹¹ Interaction constants of DeHayes and Busch,¹² as modified by Endicott et al.,¹³ were used. For all possible isomers, 43 atoms and between 450 and 495 interactions were included in the force field model. A rms coordinate shift of 0.01 Å with all nonbonded interactions at less than 3 Å included were accepted as convergence criteria. A locally modified version of ORTEP¹⁴ was used to produce the structural drawings.

Syntheses. 1,10-Diamino-2,9-dimethyl-4,7-diazadecane (3',2,3'-tet). The preparation was adapted from the method of Israel et al.¹⁵ To a solution of 15.0 g (0.25 mol) of ethylenediamine in 75 mL of benzene was added dropwise at room temperature 33.5 g (0.50 mol) of methacrylonitrile. After the addition, the reaction mixture was heated for 3 h at 70 °C and an additional 20 h at 110 °C. The benzene was removed under reduced pressure and the dinitrile 1,8-dimethyl-3,6-diaza-1,8-octanedinitrile (I) collected by vacuum distillation at 125-128 °C (0.20 mmHg); yield 40.3 g, 83%.

The dinitrile, I, was converted to the tetraamine by hydrogenation using a Parr low-pressure hydrogenation apparatus and a sponge nickel catalyst. A 30.0-g sample of the dinitrile, I, was dissolved in 175 mL of degassed ethanol that had been saturated with anhydrous ammonia. Raney nickel catalyst (Aldrich) was added and the mixture shaken overnight. The catalyst was filtered, the ethanol removed under reduced pressure, and the tetraamine distilled under vacuum (bp 89-91 °C (0.3 mm)); yield 29.1 g, 93%.

***trans*-(RSSR,SRRS)-Dichloro(1,10-diamino-2,9-dimethyl-4,7-diazadecane)cobalt(III) Perchlorate (*trans*-(RSSR,SRRS)-[Co(3',2,3'-tet)Cl₂]ClO₄) and *trans*-(RSSS,SRRR)-Dichloro(1,10-diamino-2,9-dimethyl-4,7-diazadecane)cobalt(III) Perchlorate (*trans*-(RSSS,SRRR)-[Co(3',2,3'-tet)Cl₂]ClO₄.** A solution of 4.50

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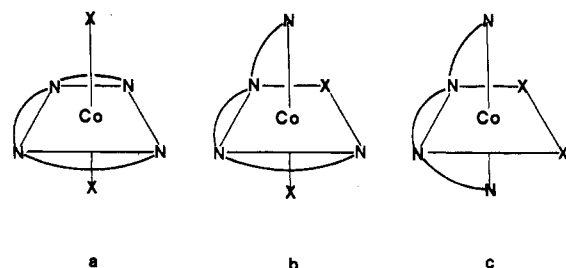


Figure 1. Topology of six-coordinate complex with flexible tetradentate ligands: (a) trans; (b) Δ -uns-cis; (c) Δ -s-cis.

g (0.023 mol) of 3',2,3'-tet and 5.47 g (0.023 mol) of cobalt(II) chloride hexahydrate in 65 mL of water was oxidized with CO₂-free air for 16 h at room temperature. Concentrated hydrochloric acid (6.5 mL) was added, and the solution was evaporated to dryness on a steam bath. The resulting solid was handled in one of two ways.

1. A 1-g portion of the solid was dissolved in a minimum of water. The resulting green solution was placed on an ion-exchange column. Elution with 0.01 M perchloric acid yielded the complex *trans*-(*RSSS,SSSR*)-[Co(3',2,3'-tet)Cl₂]ClO₄·2H₂O (derived from the meso ligand). The remaining complex, *trans*-(*RSSR,SRRS*)-[Co(3',2,3'-tet)Cl₂]ClO₄·2H₂O (derived from the racemic ligand), was eluted with 0.2 M HClO₄.

2. The solid was dissolved in a minimum amount of boiling water, cooled, and filtered. The solid contained primarily *trans*-(*RSSR,SRRS*)-[Co(3',2,3'-tet)Cl₂]Cl.

The remaining solution was evaporated to near dryness and the solid collected. The solid was primarily *trans*-(*RSSS,SRRR*)-[Co(3',2,3'-tet)Cl₂]Cl. After repetition of the above procedure the products were of greater than 95% isomeric purity as judged by NMR.

Analyses

<i>trans</i> -(<i>RSSR,SRRS</i>)-[Co(3',2,3'-tet)Cl ₂]Cl·2H ₂ O				
	C	H	N	Co
% calcd	29.71	6.44	13.86	14.52
% found	29.02	6.67	13.56	14.95
<i>trans</i> -(<i>RSSS,SRRR</i>)-[Co(3',2,3'-tet)Cl ₂]Cl·2H ₂ O				
	C	H	N	Co
% calcd	29.71	6.44	13.86	14.52
% found	29.51	6.58	13.98	14.34

Results and Discussion

Synthesis. The synthesis of the two *trans*-dichloro complexes arises as a result of the two different isomers of the ligand. Addition of ethylenediamine to methacrylonitrile to produce the dinitrile, I, should yield a statistical mixture of 50% racemic and 50% meso tetraamine ligand; we have made no attempts to separate this mixture.

Air oxidation of cobalt(II) chloride in the presence of the ligand, followed by the addition of hydrochloric acid, yields intensely green solutions characteristic of *trans*-dichloro tetraamine complexes.¹⁶ The two asymmetric carbon centers and two asymmetric nitrogen centers permit the formation of six stereochemically different *trans* isomers. In order to separate these isomers the resulting solution was placed on an ion-exchange column. Elution with 0.01 M HClO₄ produced two bands with very different mobilities. The first band, eluted with 0.01 M HClO₄, contained the *trans*-*RSSS,SRRR* complex. The second band, eluted with 0.2 M HClO₄, contained only the *trans*-*RSSR,SRRS* complex. The ion-exchange experiments showed no evidence of the remaining four combinations of chiral centers.

Electronic Spectra. The electronic spectra of these two complexes are similar to those reported for other *trans*-dichloro tetraamine complexes and were assigned by using the model proposed by Piper and Wentworth¹⁷ and applied to similar

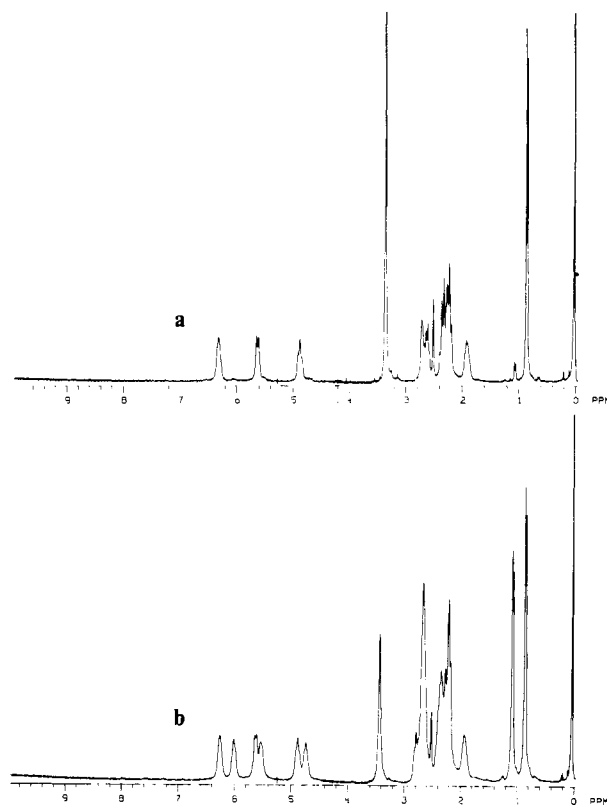


Figure 2. Proton NMR spectra of (a) *trans*-(*RSSR,SRRS*)-[Co(3',2,3'-tet)Cl₂]⁺ and (b) *trans*-(*RSSS,SRRR*)-[Co(3',2,3'-tet)Cl₂]⁺.

complexes by Brubaker and Fitzgerald.⁵ Both complexes exhibit bands assigned to ¹A_{1g} → ¹A_{2g} at 15 600 cm⁻¹ and ¹A_{1g} → ¹E_g at 22 200 cm⁻¹ in D_{4h} microsymmetry. An additional band at higher energy (27 000 cm⁻¹) is assigned to the ¹A_{1g} → ¹T_{2g} transition in octahedral symmetry.

Proton Magnetic Resonance. The 300-MHz proton NMR spectra for *trans*-(*RSSR,SRRS*)- and *trans*-(*RSSS,SRRR*)-[Co(3',2,3'-tet)Cl₂]⁺ complexes are shown in Figure 2. While the proton NMR spectra of these compounds are complex, some of the major differences provide insight into the stereochemistries of the complexes.

The simplest region of the NMR spectrum to interpret is between 6.5 and 4.0 ppm from Me₄Si. These resonances, broadened by coupling with the Co and N nuclei,^{18,19} are assigned to the amine protons of the complex. There are three signals observed for *trans*-(*RSSR,SRRS*)-[Co(3',2,3'-tet)Cl₂]⁺, consistent with the dihedral symmetry of this complex. The same region of the spectrum for *trans*-(*RSSS,SRRR*)-[Co(3',2,3'-tet)Cl₂]⁺ shows six separate resonances, each representing a single proton. Of the six resonances present for *trans*-(*RSSS,SRRR*)-[Co(3',2,3'-tet)Cl₂]⁺, three signals appear at the same chemical shift as the signals from *trans*-(*RSSR,SRRS*)-[Co(3',2,3'-tet)Cl₂]⁺ and the remaining three at lower chemical shifts, indicating an increase in ring strain.¹⁹ The observation of three and six resonances for the two complexes indicates a decrease in the symmetry of *trans*-(*RSSS,SRRR*)-[Co(3',2,3'-tet)Cl₂]⁺ compared with that of *trans*-(*RSSR,SRRS*)-[Co(3',2,3'-tet)Cl₂]⁺ and also eliminates the possibility of a rapid equilibrium among possible chelate ring conformations.¹⁹

The second major difference between the two NMR spectra is the appearance of two methyl signals in the spectrum of

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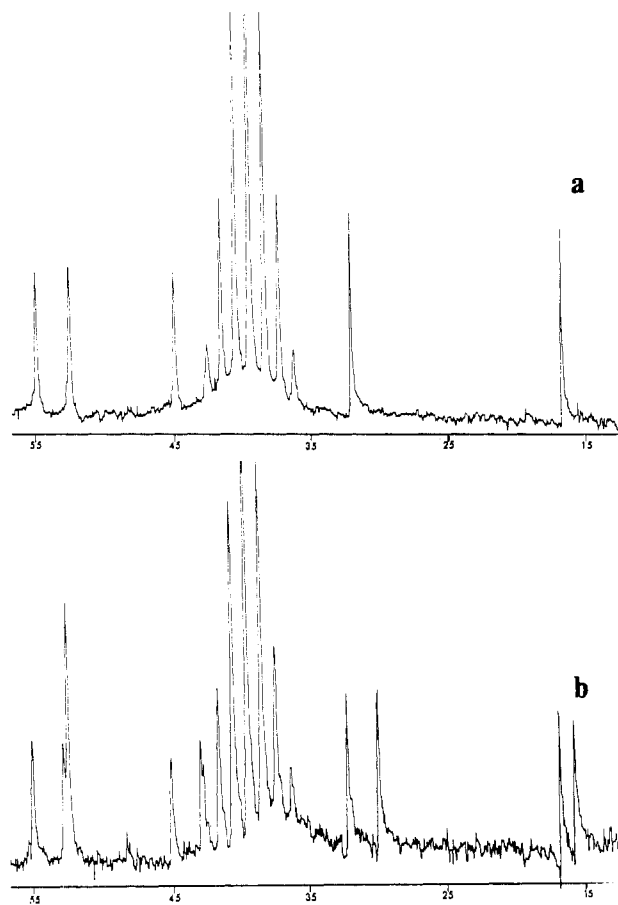


Figure 3. Carbon-13 NMR spectra of (a) *trans*-(RSSR,SRRS)-[Co(3',2,3'-tet)Cl₂]⁺ and (b) *trans*-(RSSH,SRRR)-[Co(3',2,3'-tet)Cl₂]⁺. The heptet centered at 39.5 ppm from Me₄Si arises from the solvent, Me₂SO.

trans-(RSSH,SRRR)-[Co(3',2,3'-tet)Cl₂]⁺. These different signals reflect the different environment of the methyl protons and probably also the different conformations of the six-membered chelate rings (vide infra).

The complex series of multiplets appearing between 1.8 and 2.8 ppm correspond to the protons of the five- and six-membered chelate rings.^{6,17} While a complete assignment of these signals has not been attempted, the increased complexity found in the spectrum of *trans*-(RSSH,SRRR)-[Co(3',2,3'-tet)Cl₂]⁺ is consistent with the decreased symmetry expected for this complex.

Carbon-13 NMR Spectroscopy. The carbon-13 NMR spectra of these complexes (shown in Figure 3) are characterized by excellent signal to noise ratios and narrow (5 Hz) lines. They do not appear to suffer significantly from coupling to either the Co or N nuclei.

The assignment of the carbon-13 NMR signals of these complexes is based upon the previous assignment of the NMR spectrum of the complex with the unsubstituted ligand (*trans*-[Co(3,2,3-tet)Cl₂Cl]).¹⁰ The signals appearing at 52.65 and 52.45 ppm in the two complexes are assigned to the atoms in the five-membered chelate ring. The chemical shift of these carbons is the same as seen for the five-membered chelate ring in *trans*-[Co(3,2,3-tet)Cl₂]⁺. The chemical shift of these atoms, which are relatively distant from the methyl groups, would be expected to change the least with a change in the methyl group orientation.

The carbon atoms of the six-membered chelate ring all appear at lower shielding in the complexes with 3',2,3'-tet compared with 3,2,3-tet. In *trans*-(RSSR,SRRS)-[Co(3',2,3'-tet)Cl₂Cl] these atoms appear as three peaks in the ¹³C NMR, consistent with the expected twofold symmetry

Table I. Strain Energy Minimization Results for Some *trans*-[Co(3',2,3'-tet)Cl₂]⁺ Complexes (kcal mol⁻¹)

compd	R_{ij}	θ	ϕ	NB	total
Resulting from the Racemic Ligand					
<i>trans</i> -(RSSR,SRRS)-[Co(3',2,3'-tet)Cl ₂] ⁺	2.789	6.849	0.939	7.734	18.310
<i>trans</i> -(RRRR,SSSS)-[Co(3',2,3'-tet)Cl ₂] ⁺	3.031	9.122	0.840	8.262	21.255
<i>trans</i> -(RSRR,SRSS)-[Co(3',2,3'-tet)Cl ₂] ⁺	3.612	10.025	4.788	11.945	30.369
Resulting from the Meso Ligand					
<i>trans</i> -(RSSH,SRRR)-[Co(3',2,3'-tet)Cl ₂] ⁺	3.021	8.234	0.856	8.489	20.600
<i>trans</i> -(RSRS,SRSS)-[Co(3',2,3'-tet)Cl ₂] ⁺	3.347	8.898	5.033	11.400	28.678
<i>trans</i> -(RRSS,SSRR)-[Co(3',2,3'-tet)Cl ₂] ⁺	3.223	10.301	7.879	11.836	33.239

(which is preserved in our strain energy minimization calculations). The carbons appearing at 55.05 ppm are assigned to the carbons α^{20} to a secondary amine, and the carbons at 45.06 ppm are assigned to the carbons α to the primary amine. The β -carbons appear at 32.23 ppm, and the methyl carbons appear at 16.84 ppm.

The carbon-13 NMR spectrum of *trans*-(RSSH,SRRR)-[Co(3',2,3'-tet)Cl₂Cl] shows a definite decrease in symmetry. The carbons of the five-membered chelate ring appear together at the same chemical shift as in *trans*-(RSSR,SRRS)-[Co(3',2,3'-tet)Cl₂]⁺. The carbon atoms of the six-membered chelate ring, which were equivalent in *trans*-(RSSR,SRRS)-[Co(3',2,3'-tet)Cl₂]⁺, are no longer equivalent. One of the carbons appears at an unchanged chemical shift, and the other appears more shielded. The methyl carbon is shielded by 1.07 ppm, the β -carbon by 2.23 ppm, and the α -carbons by 2.25 ppm.

The differences observed between the two methyl atoms and between the two β -carbon atoms of *trans*-(RSSH,SRRR)-[Co(3',2,3'-tet)Cl₂Cl] are much smaller than expected to result from the influence of an axial methyl group.²¹ Simple substituent additivity rules²² for substituted cyclohexanes predict a much larger chemical shift difference between an axial and an equatorial methyl group and between the carbon atoms β to such substituents. Thus, the carbon-13 NMR spectrum of *cis*-1,4-dimethylcyclohexane²³ shows a difference of about 6 ppm in the ¹³C resonance signal for the axial and equatorial methyl groups and a difference of almost 7 ppm for the signals from the carbons.²⁰

The small methyl and β -carbon chemical shift differences we have observed lead us to believe that the methyl group is not strictly in an axial position but rather in an intermediate position resulting from strong nonbonded interactions with the coordinated chloride ions. These interactions also force the chelate ring into a less ideal geometry (vide infra), leading to the larger chemical shift differences at the α -carbon atoms.

Strain Energy Minimization Calculations. Strain energy minimization calculations have been used to predict the structure of cobalt(III) complexes.^{3,8} In order to gain a better understanding of the structures of the complexes we have isolated, and understand why, of the six possible stereoisomers only two were found, we have calculated the strain energy

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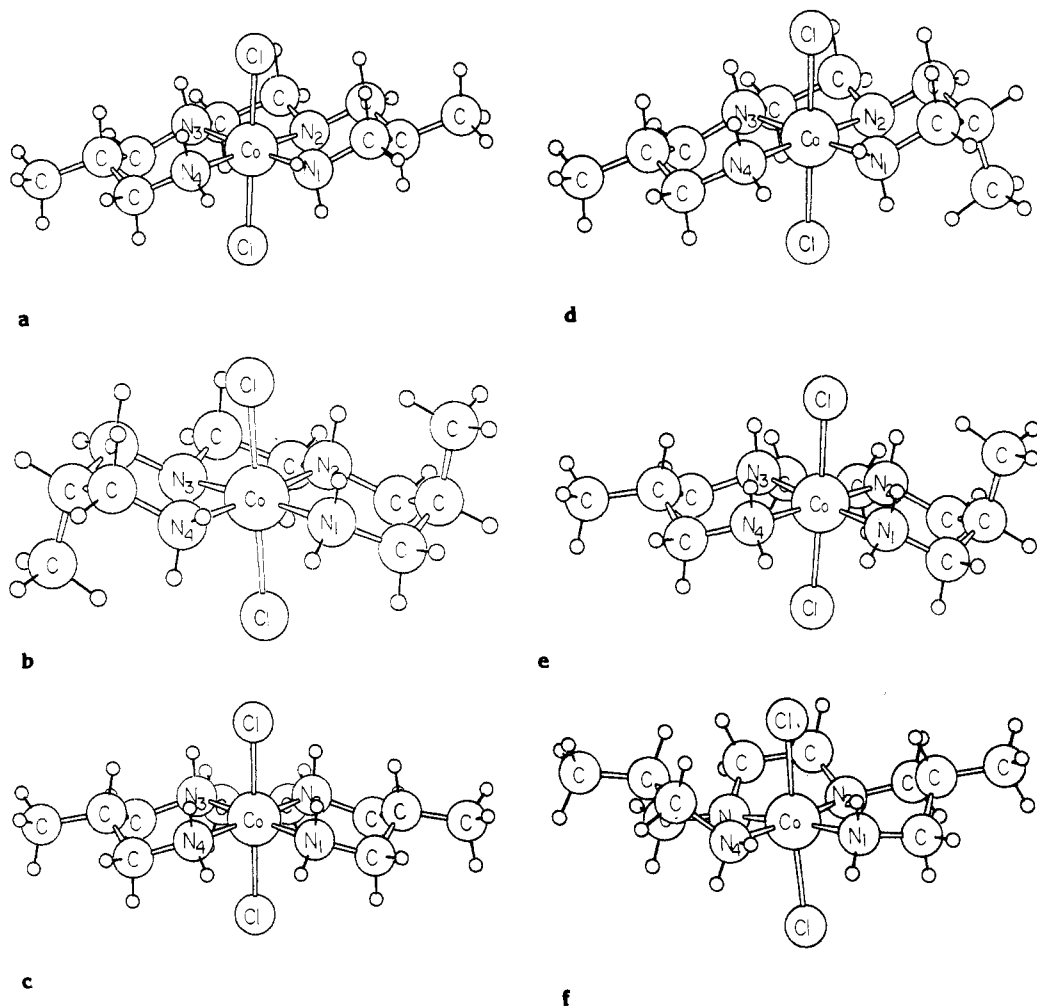


Figure 4. ORTEP drawings from the strain energy minimized coordinates for complexes from the racemic ligand [(a) *trans*-(*RSSR,SRRS*)-[Co(3',2,3'-tet)Cl₂]⁺, (b) *trans*-(*SSSS,RRRR*)-[Co(3',2,3'-tet)Cl₂]⁺, (c) *trans*-(*RSRR,SRSS*)-[Co(3',2,3'-tet)Cl₂]⁺] and from the meso ligand [(d) *trans*-(*RSSS,SRRR*)-[Co(3',2,3'-tet)Cl₂]⁺, (e) *trans*-(*RSRS,SRSR*)-[Co(3',2,3'-tet)Cl₂]⁺, (f) *trans*-(*RRSS,SSRR*)-[Co(3',2,3'-tet)Cl₂]⁺].

minimized structures of all of the possible stereoisomers. The results of these calculations are shown in Table I.

All of the calculated structures (shown in Figure 4) have reasonable chelate ring conformations for the topologies indicated. The three structures with eclipsed five-membered chelate ring conformations are the three highest strain energy structures; the three low-energy structures have gauche five-membered chelate rings.

Since the synthetic route to the free ligand (*vide supra*) results in a mixture of the meso and racemic forms (considering only the chirality of the carbon centers in the free ligand), at least two different complexes should result. The relative energies of complexes with the different stereoisomers of the racemic ligand, *trans*-(*RSSR,SRRS*)-[Co(3',2,3'-tet)Cl₂]⁺ and *trans*-(*RRRR,SSSS*)-[Co(3',2,3'-tet)Cl₂]⁺ (Table I), indicate that the former should comprise more than 99% of the product. The energy difference between these isomers, the former with two equatorial methyl groups and the latter with two axial methyl groups, is about 1.5 kcal mol⁻¹ per axial methyl group, satisfyingly close to the 1.7 kcal mol⁻¹ in methylcyclohexane. Similarly, the calculated strain energy difference between complexes of the meso ligand, *trans*-(*RSSS,SRRR*)-[Co(3',2,3'-tet)Cl₂]⁺ and *trans*-(*RSRS,SRSR*)-[Co(3',2,3'-tet)Cl₂]⁺, suggests that virtually none of the latter complex should appear in the product mixture (Table I).

All of the other possible complexes lie at even higher strain energies. Clearly, the strain energy of an eclipsed bridging five-membered ethylenediamine-like chelate ring must be greater than the 1.5 kcal mol⁻¹ or so that distinguishes an

Table II. Selected Bond Distances (Å) and Angles (deg) from the Calculated Structures of *trans*-(*RSSR,SRRS*)- and *trans*-(*RSSS,SRRR*)-Co(3',2,3'-tet) Complexes

dist or angle	<i>trans</i> -(<i>RSSR,SRRS</i>)- [Co(3',2,3'-tet)Cl ₂] ⁺	<i>trans</i> -(<i>RSSS,SRRR</i>)- [Co(3',2,3'-tet)Cl ₂] ⁺
Co-N(1)	2.00	2.00
Co-N(2)	2.00	1.99
Co-Cl(+)	2.34	2.34
Co-Cl(-)	2.34	2.34
N(1)-C(1)	1.50	1.50
C(1)-C(2)	1.53	1.53
C(2)-C(Me)	1.54	1.54
C(2)-C(3)	1.53	1.54
C(3)-N(2)	1.49	1.49
N(1)-Co-N(2)	90.9	91.1
Cl(+)-Co-Cl(-)	177.6	178.0
N(1)-Co-Cl(+)	86.8	87.1
N(1)-Co-Cl(-)	90.9	90.9
Co-N(1)-C(1)	122.3	122.5
N(1)-C(1)-C(2)	112.5	114.0
C(1)-C(2)-C(3)	110.1	110.8
C(1)-C(2)-C(Me)	109.9	112.4
C(2)-C(3)-N(2)	112.1	113.8
C(3)-N(2)-C(4)	110.4	110.2

equatorial from an axial methyl substituent on the six-membered chelate ring.

ORTEP drawings, based on the final coordinates (shown in Figure 4), show the minimum-energy structure of *trans*-(*RSSR,SRRS*)-[Co(3',2,3'-tet)Cl₂]⁺. This isomer has a structure very similar to that reported for *trans*-[Co(3,2,3-

Table III. Significant (>0.2 kcal/mol) Nonbonded Interactions Calculated for the Complexes *trans*-(*RSSR,SRRS*)- and *trans*-(*RSSS,SRRR*)-[Co(3',2,3'-tet)Cl₂]⁺

atoms	<i>trans</i> -(<i>RSSR,SRRS</i>)- [Co(3',2,3'-tet)Cl ₂] ⁺		<i>trans</i> -(<i>RSSS,SRRR</i>)- [Co(3',2,3'-tet)Cl ₂] ⁺	
	<i>D</i> , Å	energy, kcal/mol	<i>D</i> , Å	energy, kcal/mol
H(N1)-H(C1)	2.36	0.353	2.37	0.331
H(N1)-H'(C1)	2.34	0.419	2.30	0.547
H(N1)-H(N4)	2.26	0.697	2.25	0.753
H'(N1)-H(C1)	2.30	0.539	2.31	0.500
H'(N1)-Cl(-)	2.73	0.876	2.74	0.816
H'(C1)-Cl(+)	2.83	0.427	2.82	0.430
H'(C1)-H(C2)	3.05	-0.073	2.40	0.242
H(C2)-H(C(Me))	2.49	0.103	2.42	0.202
H(C2)-H(C3)	2.54	0.043	2.42	0.200
H(C(Me))-H(N2)	4.56	-0.010	2.32	0.483
H(C3)-H(N2)	2.32	0.486	2.32	0.475
H(C3)-Cl(+)	2.86	0.323	2.85	0.352
H(N2)-H(C4)	2.32	0.467	2.30	0.527
H(N2)-Cl(-)	2.69	1.095	2.85	1.080
H(C5)-H(N3)	2.32	0.467	2.32	0.482
H(N3)-H(C6)	2.32	0.487	2.31	0.495
H(N3)-Cl(+)	2.69	1.103	2.68	1.161
H(C6)-Cl(-)	2.86	0.322	2.84	0.362
H(C8)-H(N4)	2.33	0.423	2.33	0.432
H(C8)-Cl(-)	2.83	0.427	2.82	0.445
H'(C8)-H(N4)	2.36	0.355	2.35	0.370
H'(C8)-H'(N4)	2.30	0.546	2.30	0.539

tet)Cl₂]Cl²⁴ with the two methyl groups in equatorial positions at carbons 2 and 9. The structure that has the second lowest energy, *trans*-(*RSSS,SRRR*)-[Co(3',2,3'-tet)Cl₂]⁺, is very similar to the structure described above, except one of the methyl groups is nearly in an axial position.

Some selected bond distances and angles are shown in Table II. The structure of *trans*-(*RSSR,SRRS*)-[Co(3',2,3'-tet)Cl₂]⁺ shows "normal" bond distances and slightly large bond angles, almost identical with those reported for *trans*-[Co(3,2,3-tet)Cl₂]⁺, suggesting that the introduction of two equatorially substituted methyl groups has only a minor effect on the chelate ring conformations in this complex, consistent with the NMR spectra.

The energy-minimized structure of *trans*-(*RSSS,SRRR*)-[Co(3',2,3'-tet)Cl₂]⁺ shows significant changes in the details of the conformation of the six-membered chelate ring with an axial methyl group. While the bond distances are

unchanged (the difference in bond deformation strain energy is 0.232 kcal mol⁻¹, Table I), all of the bond angles of this ring have increased (bond angle deformation energy difference of 1.385 kcal mol⁻¹, Table I). In addition, many of the calculated nonbonded interactions (shown in Table III) present in this structure are not significant in the *trans*-*RSSR,SRRS* complex (the difference in nonbonded energy is 0.755 kcal mol⁻¹, Table I).

Increased bond angles indicate that the methyl group on this chelate ring is forced into a position intermediate between axial and equatorial. The increased angle deformation calculated at the carbon atoms of this chelate ring accounts for the observed increase in the shielding of these atoms relative to those in *trans*-(*RSSR,SRRS*)-[Co(3',2,3'-tet)Cl₂]⁺.

Conclusions

The ligand 2,9-dimethyl-1,10-diamino-4,7-diazadecane (3',2,3'-tet) has been synthesized, and the complexes *trans*-(*RSSR,SRRS*)-[Co(3',2,3'-tet)Cl₂]⁺ and *trans*-(*RSSS,SRRR*)-[Co(3',2,3'-tet)Cl₂]⁺ have been isolated. No other products were detected, indicating a high degree of stereoselectivity in these complexes with four chiral centers.

High-field proton NMR and ¹³C NMR spectra are consistent with a structure of *trans*-(*RSSR,SRRS*)-[Co(3',2,3'-tet)Cl₂]⁺ that is little distorted from that of the unsubstituted complex *trans*-[Co(3,2,3-tet)Cl₂]⁺. The magnetic resonance spectra of *trans*-(*RSSS,SRRR*)-[Co(3',2,3'-tet)Cl₂]⁺ are consistent with a structure with one flattened chair six-membered chelate ring on which the methyl substituent lies between an axial and an equatorial position.

Energy-minimized structures obtained from a detailed molecular mechanics study are consistent with both the observed stereoselectivity and the magnetic resonance spectra.

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Registry No. I, 85135-00-8; (3',2,3'-tet), 85134-99-2; *trans*-(*RSSR,SRRS*)-[Co(3',2,3'-tet)Cl₂]Cl, 85150-66-9; *trans*-(*RSSS,SRRR*)-[Co(3',2,3'-tet)Cl₂]Cl, 85248-57-3; *trans*-(*RSSR,SRRS*)-[Co(3',2,3'-tet)Cl₂]⁺, 85200-86-8; *trans*-(*RRRR,SSSS*)-[Co(3',2,3'-tet)Cl₂]⁺, 85200-87-9; *trans*-(*RSRR,SRSS*)-[Co(3',2,3'-tet)Cl₂]⁺, 85200-88-0; *trans*-(*RSSS,SRRR*)-[Co(3',2,3'-tet)Cl₂]⁺, 85200-89-1; *trans*-(*RSRS,SRSR*)-[Co(3',2,3'-tet)Cl₂]⁺, 85200-90-4; *trans*-(*RRSS,SSRR*)-[Co(3',2,3'-tet)Cl₂]⁺, 85200-91-5; ethylenediamine, 107-15-3; methacrylonitrile, 126-98-7.

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