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Polyazamacrocycles. 9. Characterization of Diastereoisomeric *trans*-[Co(Me$_8$[14]ane)Cl$_2$]$^+$ Complexes

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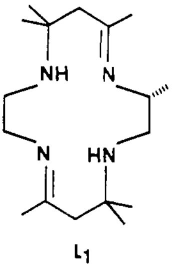
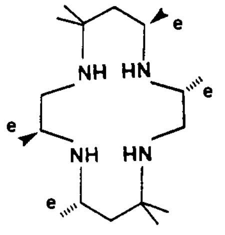
Reduction of 3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (Me$_8$[14]diene) with sodium borohydride yields three isomeric Me$_8$[14]anes (L$_A$, L$_B$, and L$_C$). These macrocycles give green *trans*-[CoLCl$_2$]ClO$_4$ diastereoisomers. It has been possible to obtain two diastereoisomers each with L$_A$ and L$_B$ and one diastereoisomer with L$_C$. These isomers give distinct infrared and ^{1}H NMR spectra. The structures of these isomers have been assigned on the basis of their ^{1}H NMR spectra. The structure of one isomer, *trans*-[CoL$_{A\alpha}$Cl$_2$]ClO$_4$, has been confirmed by X-ray crystallography.

Introduction

1,2-Propanediamine reacts with acetone to yield 3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, Me$_8$[14]diene. The reaction is stereospecific and gives only the 3,10-C-meso isomer (L$_1$). The same macrocycle has been obtained as its nickel(II) complex following a template reaction of 1,2-propanediamine with acetone. The 3,10-C-meso assignment has been established on the basis of ^{1}H NMR spectra[2,3] and confirmed by X-ray crystallography.[4] Reduction of Me$_8$[14]diene with NaBH$_4$ yields an isomeric mixture of the corresponding saturated macrocycles, Me$_8$[14]anes. This mixture has been resolved to yield three distinct isomers, Me$_8$[14]ane$_A$ (L$_A$), Me$_8$[14]ane$_B$ (L$_B$), and Me$_8$[14]ane$_C$ (L$_C$). The structures of these isomers have been established[5] on the basis of the NMR spectra. The X-ray crystallography[5] of Me$_8$[14]ane$_B$ confirms its structure as established from the NMR spectra. These macrocycles give green *trans*-[CoLCl$_2$]$^+$ complexes with cobalt(III). In principle,[6,7] owing to the presence of four chiral nitrogen centers on these macrocycles, each of the above isomeric Me$_8$[14]anes can yield 16 diastereoisomeric *trans*-[CoLCl$_2$]$^+$ complexes. Out of the 16 theoretically possible diastereoisomeric structures, only a few will be stable and abundant enough to permit their isolation in the solid state. We have been able to separate two diastereoisomers each with Me$_8$[14]ane$_A$ and Me$_8$[14]ane$_B$ and one diastereoisomer with Me$_8$[14]ane$_C$. In this paper we report the characterization of these diastereoisomers and the X-ray crystal structure of *trans*-[Co(Me$_8$[14]ane$_{A\alpha}$)Cl$_2$]$^+$.



L$_1$



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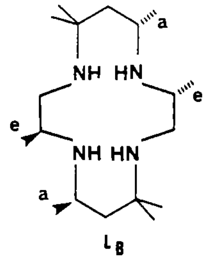
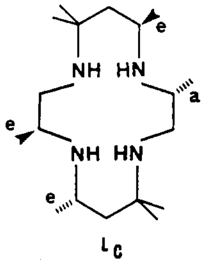
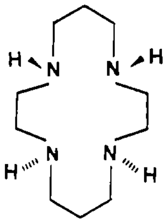


L$_B$



L$_C$



L$_2$

Experimental Section

Synthesis. Me$_8$[14]diene·2HClO$_4$ was prepared as described[2] and reduced with NaBH$_4$ in a 1:1 water–methanol mixture. The isomers Me$_8$[14]ane$_A$, Me$_8$[14]ane$_B$, and Me$_8$[14]ane$_C$ were separated by fractional crystallization from xylene.[5] The cobalt(III) complexes of these isomers were prepared by the general aeration route developed earlier[6,7] for the separation of such diastereoisomers.

Cobalt(III) Complexes of Me$_8$[14]ane$_A$. A 2.0-g (6.5 mmol) sample of the ligand and 1.61 g (6.5 mmol) of cobalt(II) acetate tetrahydrate were dissolved in 50 mL of hot methanol, and the solution was cooled and mixed. The solution was aerated till the volume reduced to ca. 20 mL. To the light brown solution was added 4 mL of concentrated HCl. Some unreacted ligand precipitated out as L$_A$·4HCl, which was redissolved by the addition of approximately 80 mL of water, and the solution was further aerated for 24 h, giving a green solution. This solution was concentrated on a steam bath till crystallization set in. On standing for a few hours, some unreacted L$_A$·4HCl and a pale green complex, [CoL$_{A\alpha}$Cl$_2$]Cl, crystallized out. The mixture was filtered off and the brown filtrate set aside for further treatment. The green product was suspended in 50 mL of ethanol and heated to dissolve the complex. The green ethanolic solution was filtered off and heated on a steam bath to approximately 60 °C, and then 1 mL of 70% HClO$_4$ was added dropwise with stirring. On cooling, a bright green complex *trans*-[CoL$_{A\alpha}$Cl$_2$]ClO$_4$ was obtained. This was recrystallized from acetonitrile, washed with ice cold ethanol and then ether, and dried in vacuo.

The brown filtrate from above was heated on a steam bath till it turned green. To this was added 1 mL of 70% HClO$_4$ dropwise, and the solution was allowed to stand at room temperature for a few hours. The green product *trans*-[CoL$_{A\beta}$Cl$_2$]ClO$_4$ was filtered off and washed with ice cold ethanol and then ether. It was finally recrystallized from acetonitrile.

Caution! Perchlorates are potentially explosive materials and should be handled with care, especially in the solid state.

Cobalt(III) Complexes of Me$_8$[14]ane$_B$. A 3.0-g (9.75 mmol) sample of the ligand and 2.42 g (9.75 mmol) of cobalt(II) acetate tetrahydrate were dissolved in 200 mL of cold methanol, and the solution was aerated for 5 h. To the deep brown solution was added 6 mL of concentrated HCl, and the volume was reduced to approximately 30 mL by bubbling with air. To the cold, deep green solution was carefully added 5 mL of 70% HClO$_4$. A green precipitate appeared immediately, which was filtered off after allowing it to stand for 1 h. The green product *trans*-[CoL$_{B\alpha}$Cl$_2$]ClO$_4$ was filtered off and washed with cold methanol

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(1) (a) University of Roorkee. (b) University of Reading.

(2) Curtis, N. F.; Swan, D. A.; Waters, T. N.; Maxwell, I. E. *J. Am. Chem. Soc.* **1969**, *91*, 4588.

(3) Ito, T.; Busch, D. H. *Inorg. Chem.* **1974**, *13*, 1770.

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Table I. Analytical and Spectral Data

complex	found^a % C	found^a % H	found^a % N	d → d band^b ν, cm^{-1} (ϵ)
$[CoL_{A\alpha}Cl_2]ClO_4$	39.88	7.45	10.26	15 280 (36)
$[CoL_{A\beta}Cl_2]ClO_4$	39.81	7.49	10.24	15 200 (42)
$[CoL_{B\alpha}Cl_2]ClO_4$	39.99	7.35	10.44	15 280 (35)
$[CoL_{B\beta}Cl_2]ClO_4$	39.78	7.35	10.46	15 360 (41)
$[CoL_{C\alpha}Cl_2]ClO_4$	39.80	7.42	10.41	15 280 (41)

^{a}Calculated for $C_{18}H_{40}N_4Cl_3O_4Co$: C, 39.88; H, 7.44; N, 10.34. ^{b}Spectra recorded in acetonitrile.

till free from acid and then with ether. The product was finally recrystallized from acetonitrile.

The filtrate from above, when heated on a steam bath for ca. 15 min, gave a green precipitate. After cooling, the complex *trans*-$[CoL_{B\beta}Cl_2]ClO_4$ was filtered off and washed with ethanol and then ether. It was recrystallized from acetonitrile.

Cobalt(III) Complex of $Me_8[14]ane_C$. A 3.0-g (9.75-mmol) sample of the ligand and 4.42 g (9.75 mmol) of cobalt(II) acetate tetrahydrate were dissolved in 90 mL of cold methanol, and the solution was aerated for 3 h to give a deep brown solution. To this was added 6 mL of concentrated HCl, and the volume was reduced to ca. 40 mL by bubbling air through the mixture. To the deep green solution was added 6 mL of 70% $HClO_4$ dropwise with stirring. It was then allowed to stand at room temperature for ca. 30 min and the dull green product *trans*-$[CoL_{C\alpha}Cl_2]ClO_4$ filtered off. It was then washed thoroughly with ethanol followed by ether and recrystallized from acetonitrile.

The filtrate from above was concentrated to approximately 5 mL on a steam bath and cooled and excess ethanol added. This gave a sticky dark green product which could not be purified to satisfactory analysis.

The infrared spectra were recorded on a Perkin-Elmer 1640 FTIR spectrophotometer. Electronic spectra were recorded on Shimadzu UV 2100 instrument. The ^1H NMR spectra were obtained in $(CD_3)_2SO$ on a Bruker WP80 90-MHz spectrometer using TMS as internal reference.

X-ray Structure Determination of $[CoL_{A\alpha}Cl_2]ClO_4$. Crystals of this isomer were prepared by slow evaporation of an acetonitrile solution of the complex.

Crystal Data. $[CoL_{A\alpha}Cl_2]ClO_4$, $CoCl_3N_4C_{18}H_{20}O_4$, $M_r = 521.4$, monoclinic, $a = 9.098$ (11) Å, $b = 15.078$ (14) Å, $c = 17.752$ (15) Å, $\beta = 93.2$ (1)°, $V = 2431.3$ Å^3, $F(000) = 1064$, $d_m = 1.48$ g cm^{-3}, $d_c = 1.48$ g cm^{-3}, $Z = 4$, Mo Kα radiation ($\lambda = 0.7107$ Å), μ (Mo Kα) = 5.45 cm^{-1}, space group $P2_1/c$.

Structure Refinement. A crystal of approximate size 0.5 × 0.33 × 0.15 mm was mounted to rotate about the α axis on a Stoe Stadi-2 diffractometer, and the data were collected via variable-width scan. Cell dimensions were obtained by measuring high-angle reflections. Background counts were 20 s, and a scan rate of 0.033° s^{-1} was applied to a width of $(1.5 + \sin \mu/\tan \theta)°$. A total of 4244 independent reflections with $2\theta < 50°$ were measured, of which 2052 in molecule A and 2256 in molecule B, both with $I > 2\sigma(I)$, were used in subsequent refinement. The structure was determined by the usual heavy-atom methods. The positions of the two independent metal atoms were determined from the Patterson function. Both occupied special positions. Remaining atoms were determined from Fourier maps. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms, isotropically in calculated positions. Hydrogen atoms were fixed in tetrahedral positions and their positions refined by full-matrix least squares to $R = 0.065$ ($R_w = 0.067$). The weighting scheme used was $w = 1/[\sigma^2(F) + 0.003F^2]$. All calculations were carried out with SHELX 76[8] and some of our own programs on the Amdahl V7 computer at the University of Reading.[9]

Results and Discussion

On the basis of their ^1H NMR spectra,[5] L_A, L_B, and L_C have been assigned the structures shown. The structure of L_B has been confirmed by X-ray crystallography.[5] These macrocyclic ligands give green *trans*-$[CoLCl_2]ClO_4$ complexes. Aeration of the methanolic solution of L_A and cobalt(II) acetate, followed by the addition of $HClO_4$, initially yields the pale green *trans*-$[CoL_{A\alpha}Cl_2]ClO_4$. Concentration of the mother liquor yields the dark green *trans*-$[CoL_{A\beta}Cl_2]ClO_4$. Likewise, L_B also gives two isomers while with L_C only one isomer could be isolated in the pure state. The N-chiral diastereoisomers in their perchlorate forms have different solubilities and could be separated by sequential precipitation during synthesis. These complexes show electronic spectra (Table I) that are fully consistent with a *trans*-$[CoLCl_2]^+$ configuration.[6,7,10] These diastereoisomers show significant differences in the fingerprint region of their IR spectra. The IR spectra exhibit all the expected characteristic bands for such complexes. The prominent ν_{NH} band appears around 3200 cm^{-1} and the perchlorate bands around 1100 and 610 cm^{-1}. The IR spectrum of each diastereoisomer is completely reproducible during their repeated synthesis.

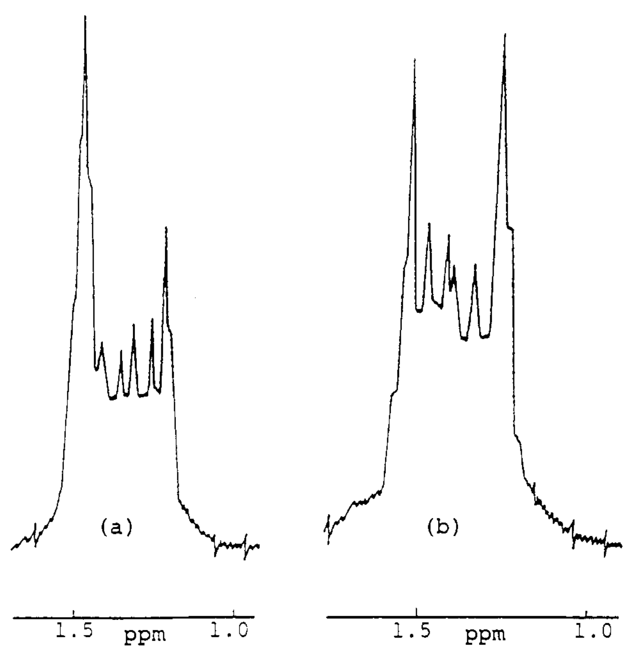

Figure 1. 90-MHz ^1H NMR spectra of (a) *trans*-$[CoL_{A\alpha}Cl_2]ClO_4$ and (b) *trans*-$[CoL_{A\beta}Cl_2]ClO_4$.

The ^1H NMR spectra of these complexes present some features that can be used to assign their configurations. The most prominent feature of these spectra would be that the geminal dimethyl groups would appear as two singlet signals, each integrating to 6 protons. The chiral methyl groups should appear as doublets. The upfield doublet near 1.2–1.3 ppm would be due to an axially oriented methyl group and the downfield doublet near 1.4–1.5 ppm due to an equatorially oriented methyl group.[11-13] The various methylene protons would appear as multiplets. On the basis of molecular models, in which the macrocyclic ring is placed in a chair form, each chiral methyl group can be assigned to be either equatorial or axial. Comparison of this expected pattern for a particular configuration with the observed pattern enables assignment of configurations to these diastereoisomers.[5-7]

The ^1H NMR spectrum of *trans*-$[CoL_{A\alpha}Cl_2]ClO_4$ (Figure 1) shows two methyl singlets at 1.23 and 1.48 ppm, which integrate to 6 H each. These can be assigned to the two pairs of *gem*-dimethyl groups placed axially and equatorially. The spectrum also shows two doublets at 1.30 and 1.39 ppm, each integrating to 6 H. These assignments were confirmed by decoupling experiments. This pattern places two of the four chiral methyls in axial positions and the other two chiral methyls in equatorial positions. The appearance of one doublet for a pair of chiral methyl groups requires them to be equivalent. This means that either the 3,10-methyls should be axial and the 5,12-methyls equatorial or vice versa. Out of the possible 16 diastereoisomeric structures, a diequatorial–diaxial arrangement is present in three

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(8) Sheldrick, G. M. *SHELX 76, Package for Crystal Structure Determination*; University of Cambridge: Cambridge, U.K., 1976.

(9) The X-ray crystallographic work was carried out at the University of Reading. Therefore, all inquiries regarding crystallographic results should be directed to this address.

(10) Bembi, R.; Roy, T. G.; Jhanji, A. K. *Inorg. Chem.* **1988**, *27*, 496.

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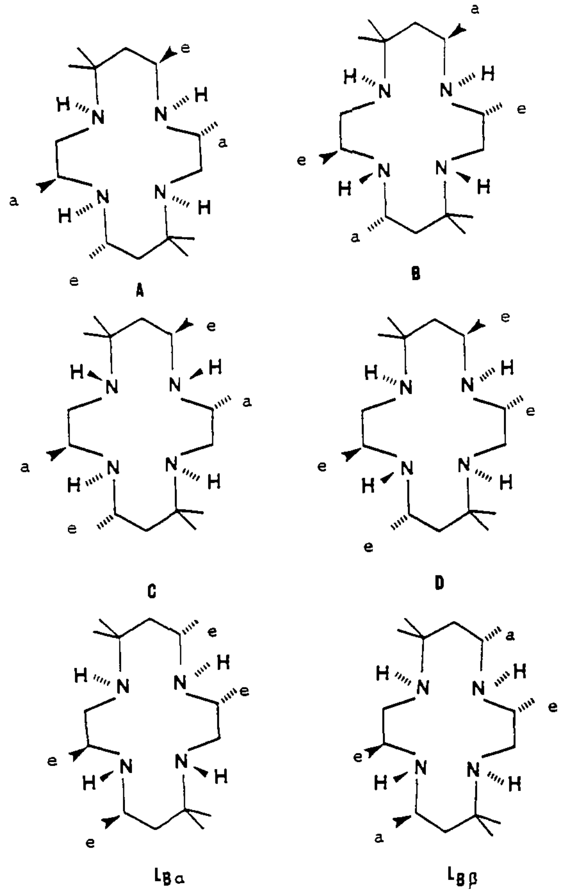
(13) Hay, R. W.; Jeragh, B. *J. Chem. Soc., Dalton Trans.* **1977**, 1261.

(14) Reference deleted in proof.

Chart I



structures, A, B, and C (Chart I). Examination of the molecular models shows that in structure A the C$_6$ methylene proton is directly oriented above the axial site and strongly hinders the formation of a six-coordinate complex. Any distortion of this structure to accommodate an axial ligand leads to instability. Both structures B and C have a trans-III type configuration of the four chiral N–H groups. The trans-III structure[15] has been shown to be the most stable configuration for [Co(cyclam)(RSRS)Cl$_2$]$^+$ (L$_2$) and other such complexes.[6,7,16] Structure B is more symmetrical and hence should be more stable and is assigned to *trans*-[CoL$_{A\alpha}$Cl$_2$]ClO$_4$. In this structure both six-membered chelate rings occupy a chair form and the two five-membered chelate rings are in gauche form. This configuration has been confirmed by our X-ray crystallographic work.

In the case of [CoL$_{A\beta}$Cl$_2$]ClO$_4$, two methyl singlets are observed at 1.27 and 1.53 ppm for the *gem*-dimethyl groups (Figure 1). The spectrum also shows two doublets at 1.38 and 1.44 ppm. These correspond to an equatorial arrangement for all the four chiral methyl groups. This arrangement is present only in structure D (Chart I), where one six-membered chelate ring attains a half-chair (twist) conformation while the other six-membered chelate ring is in the chair form. This configuration is in the logical sequence of interconversion of diastereoisomeric configurations in the sense that conversion of the most stable trans-III structure to the next should involve epimerization of only one chiral NH group.[6,7]

The ^{1}H NMR spectrum of *trans*-[CoL$_{B\alpha}$Cl$_2$]ClO$_4$ (Figure 2) shows two methyl singlets at 1.28 and 1.50 ppm and two doublets at 1.37 and 1.44 ppm. Each doublet integrates to 6 protons, and this places all the four chiral methyls in an equatorial position. This pattern is assignable to L$_{B\alpha}$. The ^{1}H NMR spectrum of *trans*-[CoL$_{B\beta}$Cl$_2$]ClO$_4$ shows closely spaced signals in two regions (Figure 2), each corresponding to 12 protons. In the first region the spectrum shows a singlet at 1.27 ppm (axial components of the *gem*-dimethyl groups) and a doublet at 1.29 ppm (pair of equivalent, axially oriented chiral methyl groups). In the second region, the spectrum shows a singlet at 1.52 ppm (equatorial components of the *gem*-dimethyl groups) and a doublet at 1.50 ppm (pair of equivalent, equatorially placed chiral methyl groups). A diequatorial–diaxial arrangement is assigned to L$_{B\beta}$.

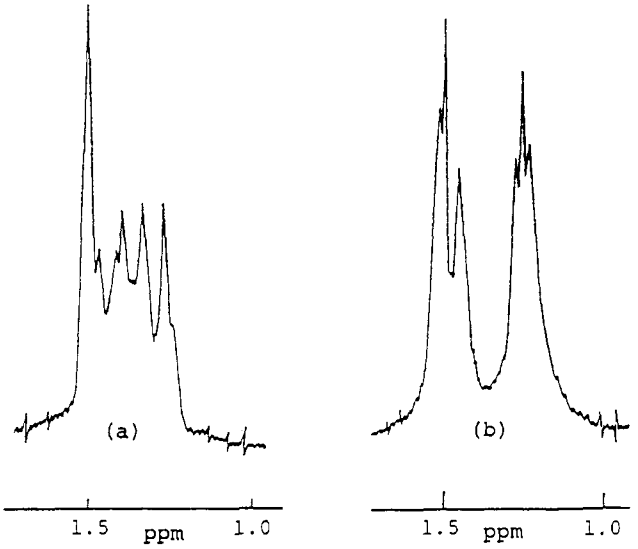


Figure 2. 90-MHz ^{1}H NMR spectra of (a) *trans*-[CoL$_{B\alpha}$Cl$_2$]ClO$_4$ and (b) *trans*-[CoL$_{B\beta}$Cl$_2$]ClO$_4$.

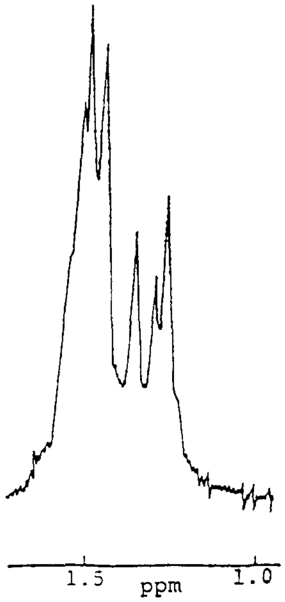


Figure 3. 90-MHz ^{1}H NMR spectrum of *trans*-[CoL$_{C\alpha}$Cl$_2$]ClO$_4$.

The ^{1}H NMR spectrum of *trans*-[CoL$_{C\alpha}$Cl$_2$]ClO$_4$ (Figure 3) shows two singlets at 1.27 and 1.50 ppm and two doublets at 1.33 and 1.48 ppm. The position of the doublets requires a diequatorial–diaxial arrangement for the chiral methyl groups. Note that both L$_A$ and L$_C$ have the same relative disposition of the four chiral methyl groups with respect to the N$_4$ plane. In the free state L$_A$ and L$_C$ differ only in their relative ring conformations.[5] Thus the diastereoisomeric forms that can be written for the complexes of L$_C$ will be identical with the ones for L$_A$. This complex can, therefore, have structure A, B, or C (Chart I). Structure A has already been ruled out and structure B assigned to *trans*-[CoL$_{A\alpha}$Cl$_2$]ClO$_4$, which has a ^{1}H NMR spectrum (Figure 1) distinct from that of *trans*-[CoL$_{C\alpha}$Cl$_2$]ClO$_4$ (Figure 3). The infrared spectra of these two isomers are also distinct. Therefore, *trans*-[CoL$_{A\alpha}$Cl$_2$]ClO$_4$ is assigned structure C. This also has a trans-III type structure and hence is a stable configuration. The X-ray structure[17] of [NiL$_{C\alpha}$](ClO$_4$)$_2$ reveals the same configuration

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[15] Bosnich, B.; Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1965**, *4*, 1102.

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Table II. Positional ($\times10^4$) and Thermal ($\times10^3$) Parameters for *trans*-[Co(Me_8[14]$ane_{A\alpha}$)Cl_2]ClO_4

atom	*x*	*y*	*z*	*U*, Å^2
Co(1A)	10000	5000	5000	47 (2)
Co(1B)	5000	5000	5000	49 (2)
N(1A)	10820 (8)	4219 (5)	4214 (4)	52 (8)
C(2A)	10729 (9)	4693 (6)	3460 (5)	55 (9)
C(3A)	9236 (10)	5142 (6)	3443 (5)	66 (10)
N(4A)	9156 (8)	5721 (5)	4118 (4)	53 (7)
C(5A)	7790 (9)	6292 (6)	4127 (5)	53 (9)
C(6A)	7846 (9)	6794 (6)	4886 (5)	59 (10)
C(7A)	7786 (9)	6314 (6)	5647 (5)	57 (10)
C(8A)	10914 (11)	4104 (7)	2774 (5)	64 (11)
C(9A)	6390 (9)	5754 (7)	3975 (5)	60 (11)
C(10A)	7873 (11)	6996 (11)	3506 (5)	67 (11)
C(11A)	6379 (10)	5827 (7)	5783 (5)	68 (11)
N(1B)	5482 (8)	5574 (5)	1009 (4)	48 (8)
C(2B)	4290 (10)	6209 (6)	1164 (5)	57 (10)
C(3B)	3824 (10)	6653 (7)	429 (5)	66 (11)
N(4B)	3446 (7)	5940 (5)	−137 (4)	53 (8)
C(5B)	2774 (10)	6277 (6)	−890 (5)	62 (11)
C(6B)	2597 (10)	5492 (7)	−1429 (5)	60 (11)
C(7B)	3892 (11)	4928 (7)	−1668 (5)	68 (11)
C(8B)	4742 (13)	6906 (8)	1750 (6)	71 (13)
C(9B)	1215 (11)	6612 (8)	−757 (7)	66 (13)
C(10B)	3706 (13)	7024 (7)	−1180 (6)	70 (12)
C(11B)	5067 (11)	5400 (8)	−2112 (6)	76 (12)

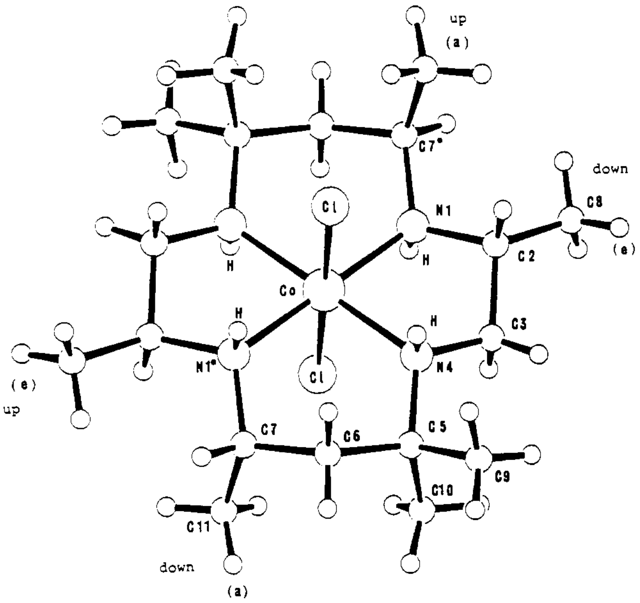

Figure 4. ORTEP perspective view of *trans*-[$CoL_{A\alpha}Cl_2$]ClO_4. Atoms are represented at the 30% probability level.

as is present in structure C (Chart I).

X-ray Structure of *trans*-[$CoL_{A\alpha}Cl_2$]ClO_4. The X-ray structure determination shows that the unit cell contains two independent *trans*-[$CoL_{A\alpha}Cl_2$]ClO_4 cations, both with crystallographically imposed centrosymmetric positions, together with a perchlorate anion in a general position. The bond length data are given in Table III.

The environment around the cobalt atoms is approximately octahedral with independent bond lengths in cation A of Co–N 2.002 (7), 2.020 (7) Å; Co–Cl 2.279 (2) Å and in cation B of Co–N 2.015 (7), 2.008 (7) Å; Co–Cl 2.275 (3) Å. These dimensions are expected for similar complexes. The conformations of the two cations are very similar, as exemplified by the torsion angles (Table V).

Table III. Bond Distances for *trans*-[Co(Me_8[14]$ane_{A\alpha}$)Cl_2]ClO_4

	dist, Å	
	molecule A	molecule B
Co(1)–N(1)	2.001 (7)	2.016 (7)
Co(1)–N(4)	2.021 (7)	2.007 (7)
Co(1)–Cl(1)	2.279 (2)	2.275 (2)
N(1)–C(2)	1.516 (11)	1.483 (12)
N(1)–C(7*)	1.510 (7)	1.482 (7)
C(2)–C(3)	1.517 (13)	1.507 (13)
C(2)–C(8)	1.524 (13)	1.519 (14)
C(3)–N(4)	1.488 (11)	1.498 (12)
N(4)–C(5)	1.513 (11)	1.525 (11)
C(5)–C(6)	1.544 (12)	1.525 (14)
C(5)–C(9)	1.521 (12)	1.537 (14)
C(5)–C(10)	1.535 (13)	1.517 (15)
C(6)–C(7)	1.536 (13)	1.531 (14)
C(7)–C(11)	1.507 (13)	1.538 (15)

Table IV. Bond Angles for *trans*-[Co(Me_8[14]$ane_{A\alpha}$)Cl_2]ClO_4

	angle, deg	
	molecule A	molecule B
N(1)–Co(1)–N(4)	85.21 (28)	85.48 (28)
N(1)–Co(1)–Cl(1)	86.71 (21)	86.36 (21)
N(4)–Co(1)–Cl(1)	94.27 (20)	94.22 (21)
Co(1)–N(1)–C(2)	109.6 (5)	108.5 (5)
Co(1)–N(1)–C(7*)	122.8 (4)	122.4 (4)
C(2)–N(1)–C(7*)	113.5 (5)	116.0 (5)
N(1)–C(2)–C(3)	103.5 (6)	107.4 (7)
N(1)–C(2)–C(8)	115.4 (7)	113.6 (7)
C(3)–C(2)–C(8)	112.6 (7)	109.7 (7)
C(2)–C(3)–N(4)	109.3 (6)	107.7 (7)
Co(1)–N(4)–C(3)	106.0 (5)	107.0 (5)
Co(1)–N(4)–C(5)	125.1 (5)	125.9 (5)
C(3)–N(4)–C(5)	114.8 (6)	114.5 (6)
N(4)–C(5)–C(6)	107.5 (6)	108.4 (6)
N(4)–C(5)–C(9)	112.0 (7)	107.7 (7)
C(6)–C(5)–C(9)	113.8 (7)	106.6 (7)
N(4)–C(5)–C(10)	108.3 (6)	109.9 (7)
C(6)–C(5)–C(10)	106.7 (7)	113.9 (8)
C(9)–C(5)–C(10)	108.4 (7)	110.3 (8)
C(5)–C(6)–C(7)	122.4 (7)	123.2 (7)
C(6)–C(7)–C(11)	116.3 (7)	116.9 (8)
C(6)–C(7)–N(1*)	108.9 (6)	109.5 (7)
C(11)–C(7)–N(1*)	115.3 (7)	113.2 (7)

Table V. Torsion Angles for *trans*-[Co(Me_8[14]$ane_{A\alpha}$)Cl_2]ClO_4

	angle, deg[a]	
	molecule A	molecule B
N(1)–C(2)–C(3)–N(4)	56.3	53.9
C(2)–C(3)–N(4)–C(5)	173.2	173.0
C(3)–N(4)–C(5)–C(6)	176.2	174.3
N(4)–C(5)–C(6)–N(7)	−64.2	−60.4
C(5)–C(6)–C(7)–N(1*)	56.3	67.3
C(6)–C(7)–N(1*)–C(2*)	177.6	175.3
C(7)–N(1*)–C(2*)–C(3*)	−177.9	−179.4
C(8)–C(2)–C(3)–C(4)	−178.5	−177.8

[a] Standard deviations are 1°

The chiral hydrogens have a trans-III type arrangement, with two chiral methyls axial and the other two chiral methyls equatorial (Figure 4), as was predicted on the basis of the ^{1}H NMR spectra. The perchlorate anion is hydrogen-bonded to one NH group (namely O(2) and N(1), O···H 2.26 Å) with a normal O···N distance of 3.13 Å.

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Supplementary Material Available: Tables of crystal data, anisotropic and isotropic thermal parameters, atomic coordinates, and bond distances and angles (9 pages); listings of structure factors (18 pages). Ordering information is given on any current masthead page.

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