bond distance. [Zn(S-*p*-tolyl)$_2$(phen)] was used as a model compound for a recent EXAFS study of the Zn center in TFIIIA.[6c] It is to be expected that the metal-ligand distances in a Zn(cys-*S*)$_2$(his)$_2$ protein center will more closely approach those found in **1**. The bond distances in **1** are also similar to those reported for bis(2-amino-1,1-dimethylethanethiolato)zinc(II) (Zn-S = 2.297 Å, Zn-N = 2.06 Å).[25a]

A similar trend in bond distances is seen in related Co(II) complexes. The Co-S and Co-N distances in [Co(S-2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$(py)$_2$] are 2.263 (9) and 2.038 (11) Å.[13] In comparison, the Co-S bond distances (2.244 (2) Å) in [Co(S-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$(2,9-Me$_2$phen)[14] are 0.02 Å shorter and the Co-N distances (2.055 (5) Å) are 0.02 Å longer. It is worthwhile to compare the M-L distances observed in the series of mixed-ligand complexes [M(SR)$_x$(imid)$_{4-x}$] with the homoleptic compounds [M(SR)$_4$]$^{2-}$ and [M(imid)$_4$]$^{2-}$ (Table VI). The entries in the tables were limited to complexes with monodentate thiolate and aromatic nitrogen ligands or polydentate ligands that do not severely distort the L-M-L angles from tetrahedral. For each metal ion, the M-S and M-N distances depend on the number of N and S donors. Increasing the number of nitrogen donors in the MS$_x$N$_{4-x}$ center results in a shortening of the M-S bonds. Increasing the number of sulfurs leads to a lengthening of the M-N bond distances. The structural data support the idea that steric repulsions between the donor atoms can perturb the M-L bond distances in tetrahedral ML$_4$ complexes.

Another possible explanation for the data is as follows: as one considers the series [M(imid)$_4$]$^{2+}$ to [M(SR)$_4$]$^{2-}$, the M-N and M-S bonds increase in length due to the change in the overall charge on the metal complex. This hypothesis does not account for the changes in the M-L distances in **1** and **2**. Also, the Co-S bonds (2.305 (13) Å) in [Co(Me$_3$AsS)$_4$]$^{2+}$ are only slightly shorter than those in [Co(SPh)$_4$]$^{2-}$.[23,24] There is a further question of the possible effect of alkyl versus aromatic thiolate ligands on M-S bond distances. Monomeric tetrahedral complexes of Zn, Cd, and Co with alkanethiolate ligands are scarce.[25] A comparison of the series of bis(1,2-ethanedithiolate) complexes, [M(edt)$_2$]$^{2-}$, with the [M(SPh)$_4$]$^{2-}$ complexes reveals no differences in the Zn-S and Cd-S distances but a shorter Co-S bond distance (2.284 (6) Å) in [Co(edt)$_2$]$^{2-}$.[23,26] Further examples of structurally characterized alkanethiolate complexes are necessary since they provide the best structural models for metal-cysteine coordination.

Although the differences in the Zn-S distances in the various [Zn(SR)$_x$(N)$_{4-x}$] centers are small, the differences are within the accuracy of EXAFS measurements on metalloproteins. It may be possible to estimate the number of cysteines bonded to a zinc center in a metalloprotein by measuring the Zn-S distance.

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Registry No. **1**, 112043-95-5; **2**, 112043-96-6.

Supplementary Material Available: Tables of thermal and hydrogen atom positional parameters and tables of bond distances and angles for **1** and **2** (10 pages); tables of structure factors for **1** and **2** (16 pages). Ordering information is given on any current masthead page.

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(27) HS-2,4,6-*i*-Pr$_3$C$_6$H$_2$ = 2,4,6-triisopropylbenzenethiol, HS-2,6-*i*-Pr$_2$C$_6$H$_3$ = 2,6-diisopropylbenzenethiol, HS-2,3,5,6-Me$_4$C$_6$H = 2,3,5,6-tetramethylbenzenethiol, imid = imidazole, 1-Me-imid = 1-methylimidazole, 2,9-Me$_2$phen = 2,9-dimethyl-1,10-phenanthroline, and bpy = 2,2′-bipyridine.

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Copper(II), Nickel(II), and Cobalt(III) Complexes with New Macrocyclic Ligands. 6,14-Dimethyl-1,5,9,13-tetraazacyclohexadeca-5,13-diene (Me$_2$[16]diene) and *C-meso*- and *C-rac*-6,14-Dimethyl-1,5,9,13-tetraazacyclohexadecane (*C-meso*- and *C-rac*-Me$_2$[16]ane)

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The new macrocyclic ligand 6,14-dimethyl-1,5,9,13-tetraazacyclohexadeca-5,13-diene, Me$_2$[16]diene, can be synthesized by the nontemplate condensation of 1,3-propanediamine monohydroperchlorate and methyl vinyl ketone at −10 °C under anhydrous conditions. Me$_2$[16]diene on reduction with sodium borohydride gives *C-meso*- and *C-rac*-Me$_2$[16]ane. The macrocycles undergo facile complexation with copper(II), nickel(II), and cobalt(III). The cobalt complexes [CoLCl$_2$]$^+$ undergo rapid thermal aquation. The high rates of aquation have been discussed in terms of the ability of the macrocycle to fold.

Introduction

The nontemplate synthesis of Me$_6$[14]diene (I, Chart I) from ethylenediamine monohydroperchlorate and acetone was first reported by Curtis and Hay.[1] By similar procedures, a variety of other tetraaza macrocycles with 13, 14, and 15 members have been prepared by the reaction of polyamines with carbonyl compounds.[2-7] Reactions of 1,4-butanediamine and 1,6-hexanedi-

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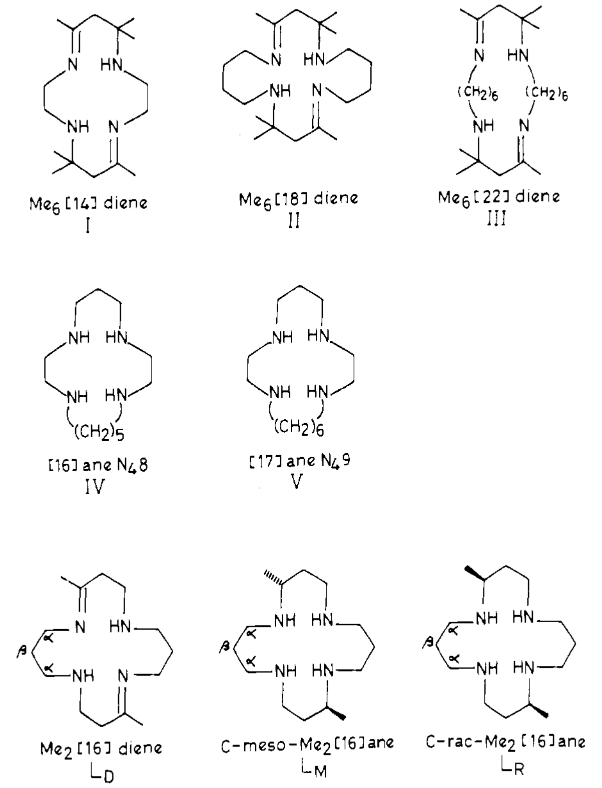
Chart I



Me_6[14] diene I, Me_6[18] diene II, Me_6[22] diene III, [16] ane $N_4$8 IV, [17] ane $N_4$9 V, Me_2[16] diene L_D, C-meso-Me_2[16]ane L_M, C-rac-Me_2[16]ane L_R

amine[9,10] with acetone have yielded macrocycles with 18 and 22 members, II and III. Attempts to prepare other ring sizes with greater than 15 members by similar methods have not been successful so far.

The larger sized rings are especially interesting from the view point of the stability of their complexes.[11] The stability of tetraaza macrocyclic complexes appears to be dependent on the cavity size, the chelate ring size, and the sequence of the chelate ring size. It has been observed that the sequence 5,6,5 of the chelate ring size is ideal for high stability.[12] This holds the four donor nitrogen atoms in a "preoriented" geometry favorable for coordination. In order to have a further insight into the stability of larger ring macrocyclic complexes, we have been involved in attempts to synthesize such macrocycles. We have now prepared the 16-membered ring compound Me_2[16]diene (L_D) by the nontemplate reaction of 1,3-propanediamine with methyl vinyl ketone. The reduction products of this macrocycle, viz., *C-meso-* and *C-rac-*Me_2[14]ane (L_M and L_R, respectively), have also been isolated. In this paper we report the synthesis of these ligands and results of our studies on complexes of copper(II), nickel(II), and cobalt(III) with them.

Table I. Elemental Analyses for the Complexes

compd[a]	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found
$[CuL_D](ClO_4)_2$	33.66	33.14	5.48	5.64	10.88	10.99
$[NiL_D](ClO_4)_2$	32.97	33.19	5.53	5.59	10.98	10.99
$[CoL_DCl_2]ClO_4$	34.95	34.91	5.87	5.93	11.64	11.51
$[CoL_D(NO_2)Cl]ClO_4$	34.16	34.00	5.73	5.75	14.22	14.33
$[CoL_D(NO_2)_2]ClO_4$	33.44	33.24	5.61	5.51	16.71	16.75
$[CoL_D(H_2O)_2](ClO_4)_3$	26.04	26.21	4.99	5.21	8.67	8.71
$[CuL_M](ClO_4)_2$	32.41	32.49	6.22	6.21	10.80	10.83
$[CuL_R](ClO_4)_2$	32.41	32.43	6.22	6.19	10.80	10.76
$[NiL_M](ClO_4)_2$	32.71	32.77	6.27	6.28	10.90	10.94
$[NiL_R](ClO_4)_2$	32.71	32.75	6.27	6.21	10.91	10.90
$[CoL_MCl_2]ClO_4$	34.62	34.70	6.64	6.72	11.53	11.41
$[CoL_RCl_2]ClO_4$	34.62	34.71	6.64	6.60	11.53	11.62

[a] Legend: $L_D = C_{14}H_{28}N_4$; $L_M = L_R = C_{14}H_{32}N_4$.

Experimental Section

Synthesis. Me_2[16]diene, L_D. The macrocyclic ligand Me_2[16]diene, as its dihydroperchlorate, was prepared essentially by the method described by Kolinski,[7] with some modifications. A 10-g quantity of 1,3-propanediamine was converted to its dihydroperchlorate by reacting with 70% $HClO_4$. The product was dried for several weeks in a vacuum desiccator over anhydrous calcium chloride. A 27.5-g (0.1-mol) portion of the dry dihydroperchlorate ws suspended in 200 mL of absolute ethanol in a 500-mL round-bottom flask. To this was added 7.4 g (0.1 mol) of anhydrous 1,3-propanediamine (freshly distilled over KOH) dropwise with magnetic stirring. The solvent was then distilled off on a rotary evaporator. The last trace of moisture was removed by azeotropic distillation (ethanol–benzene). To the anhydrous 1,3-propanediamine monohydroperchlorate was added 100 mL of absolute ethanol, and the mixture was cooled to −10 °C. A 7.0-g (0.1-mol) portion of methyl vinyl ketone cooled to −10 °C was then added dropwise over a period of 2 h with constant stirring. The flask was then tightly stoppered; the mixture was allowed to warm to 0 °C in about 2 h and left in the refrigerator overnight. The straw-colored sticky product that deposited in the flask was separated by decantation and washed several times with ice-cold ether. The product is highly hygroscopic and unstable. It can be stored at around 0 °C for a few hours without any apparent change, after which it starts changing into a dark brown viscous liquid. The product was immediately subjected to reduction with sodium borohydride and preparation of its complexes; yield about 3 g.

Me_2[16]anes, L_M and L_R. A 10-g amount of the above ligand was suspended in 50 mL of a 50% water–50% methanol mixture and reduced by the slow addition of 2.5 g of sodium borohydride. Methanol was removed on a rotary evaporator and the pH of the solution raised to above 12 with saturated NaOH solution. The reduced ligand, an isomeric mixture of the *C-meso* and *C-rac* forms, was then extracted with several portions of warm chloroform. The extracts were dried with anhydrous sodium sulfate and evaporated to dryness, leaving behind a brownish viscous mass, which changes to a glassy solid overnight. The product was dissolved in the minimum amount of hot xylene and then left overnight. *C-meso*-Me_2[16]ane, which settles as a red viscous material, was separated by decantation and washed several times with cold xylene followed by ether. It was purified by repeating the procedure with another aliquot of xylene and finally dried under vacuum.

The decanted xylene solution was left to evaporate at ambient temperature for several days when a yellow product, *C-rac*-Me_2[16]ane, was deposited. The product was separated by decantation and washed several times with ether. It was further purified by recrystallization from the minimum amount of xylene, as above, and then dried under vacuum.

$[CuL_D](ClO_4)_2$ and $[NiL_D](ClO_4)_2$. A 1.0-g amount of the ligand L_D was suspended in 200 mL of a 50% water–50% methanol mixture and 1.5 g of copper(II) carbonate added to it. After it was stirred well, the mixture was heated on a steam bath for ca. 10 min and allowed to stand for 1 h. The unreacted copper(II) carbonate was filtered and the deep blue filtrate dried on a steam bath. The blue residue was recrystallized from methanol, washed with ether, and dried under vacuum.

$[NiL_D](ClO_4)_2$ was similarly prepared by reacting the ligand with nickel(II) carbonate and heating for 1 h.

$[CoL_DCl_2]ClO_4$. A 2.0-g portion of L_D was suspended in 50 mL of a 50% water–50% methanol mixture and 2.0 g of freshly prepared sodium tris(carbonato)cobaltate(III)[13] added to it. The mixture was heated on a steam bath until it turned red (ca. 30 min). A 100-mL aliquot of concentrated HCl was added slowly and the solution further heated for 10 min. To the deep green solution was added 2 mL of 70% $HClO_4$ and the volume reduced on a steam bath until crystallization set in. When the mixture stood for a few hours, a green product deposited, which was filtered, washed with ethanol and ether, and dried under vacuum.

$[CoL_D(Cl)NO_2]ClO_4$. A 0.48-g portion of $[CoL_DCl_2]ClO_4$ and 0.08 g of $NaNO_2$ in 20 mL of methanol were heated at 60 °C with stirring

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Table II. ^1H NMR Resonance Data[a]

compd	Me(e)	Me(a)	α-CH_2	β-CH_2	coupled H
C-meso-Me_2[16]ane[b]	1.50 d (J = 6.0 Hz, 3 H)	1.68 d (J = 7.3 Hz, 3 H)	3.38 s (12 H)	2.40 s (8 H)	3.90 (2 H)
C-rac-Me_2[16]ane	1.50 d (J = 6.0 Hz, 6 H)		3.36 s (12 H)	2.40 s (8 H)	3.90 (2 H)
[CoL_DCl_2]ClO_4[c]	1.80 s (6 H)		3.47 s (12 H)	2.63 (8 H)	

[a] All chemical shifts are in ppm downfield from internal trimethylsilane. Abbreviations: d, doublet; s, singlet; e, equatorial; a, axial. [b] 400-MHz spectra. [c] 90-MHz spectra.

until a violet color developed. A 50-mg amount of $LiClO_4$ was added and the hot solution filtered. The volume of the filtrate was reduced to 10 mL, and the mixture was allowed to stand for a few hours. The violet product was filtered, washed with ether, and dried under vacuum.

[$CoL_D(NO_2)_2$]ClO_4. A 0.48-g portion of [CoL_DCl_2]ClO_4 and 0.18 g of $NaNO_2$ in 25 mL of methanol were heated at 60 °C with stirring until a deep yellow color developed. A 50-mg amount of $LiClO_4$ was added and the hot solution filtered. The volume of the filtrate was reduced to 10 mL, and the mixture was allowed to stand for a few hours. The yellow product was filtered, washed with ether, and dried under vacuum.

[$CoL_D(H_2O)_2$]$(ClO_4)_3$. A 0.5-g portion of [CoL_DCl_2]ClO_4 and 1.0 g of moist AgOH suspended in 10 mL of water were heated for about 10 min on a steam bath and allowed to stand in the dark overnight. The insoluble AgOH and AgCl were filtered, and the red filtrate was neutralized with dilute $HClO_4$ to a pH between 4.0 and 5.0. The solution was then taken to dryness on a steam bath and the red product dried under vacuum.

[CuL_M]$(ClO_4)_2$ and [CuL_R]$(ClO_4)_2$. A 2-mmol portion of the ligand and 2 mmol of copper(II) perchlorate in 10 mL of methanol were heated for about 10 min. A greenish blue sticky product separates on cooling. The mother liquor was decanted and the product washed with ethanol. It was recrystallized once from methanol, washed with ethanol and ether, and dried under vacuum.

[NiL_M]$(ClO_4)_2$ and [NiL_R]$(ClO_4)_2$. A 2-mmol portion of the ligand and 2 mmol of nickel(II) acetate were dissolved in a 90% water–10% methanol mixture and heated on a steam bath until the solution became yellow (about 3 h for L_M and 18 h for L_R). To this was added 2.5 mmol of $LiClO_4$ and the volume reduced to ca. 2 mL. The yellow nickel(II) complex was precipitated from this solution by adding 5 mL of ethanol, followed by excess ether. The product was quickly filtered, washed with ether, and dried under vacuum.

[CoL_MCl_2]ClO_4 and [CoL_RCl_2]ClO_4. A mixture of 5 mmol of the ligand and 5 mmol of cobalt(II) acetate dissolved in 200 mL of methanol was aerated overnight by bubbling air through it. To the red solution was added 10 mL of concentrated HCl, and the mixture was heated until it turned green. A 2-mL of aliquot of 70% $HClO_4$ was added and the volume reduced to about 10 mL on a steam bath. When this mixture stood, a green sticky product deposited, which was separated by decantation. The product was washed with ethanol and ether and dried under vacuum. The product is hygroscopic and quickly turns red with addition of water.

[Co([16]ane$N_4$8)Cl_2]ClO_4 and [Co([17]ane$N_4$9)]ClO_4 were prepared as described.[11]

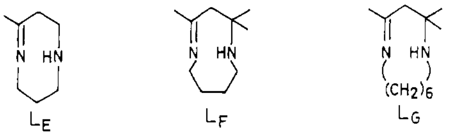
Measurements. Infrared spectra of the complexes were recorded as disks in KBr and spectra of the ligands in chloroform with NaCl cells on a Beckman IR 20 spectrophotometer. Routine spectra were recorded with a Beckman DU-6 spectrophotometer. Conductance measurements at 25 ± 0.1 °C were carried out on a Systronics conductivity bridge, Type 302. ^1H NMR spectra (90 MHz) were recorded with a Bruker WP80 instrument in $(CD_3)_2SO$ with trimethylsilane as internal reference. The 400-MHz ^1H NMR and mass spectra were recorded at the Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow, India. The ^1H NMR spectra were recorded in trifluoroacetic acid as solvent with trimethylsilane as reference.

Interval-scan spectra were recorded on a Carl Zeiss Specord spectrophotometer. Aquation kinetics were monitored spectrophotometrically with a Beckmann DU-6 instrument in the kinetics mode. The kinetic data were computed on a DEC 20 computer system. All aquation studies were carried out in 0.1 M $HClO_4$. The reported rates are an average of at least three runs each showing a correlation coefficient of 0.999 calculated over more than 3 half-lives.

Results and Discussion

Syntheses of Ligands. The results of these studies show that the 16-membered macrocycle Me_2[16]diene can be readily obtained by reaction of methyl vinyl ketone with 1,3-propanediamine monohydroperchlorate under anhydrous conditions. The ligand is highly unstable and decomposes within a few hours of its isolation even at low temperatures. The ligand was therefore immediately reduced to the corresponding saturated macrocycle or converted into its metal complexes. The high instability prevented analytical, IR, or NMR measurements on the ligand. The free ligand probably exists as an 8-membered diaza ring, L_E (Chart II), instead of a 16-membered ring. The high instability could then be correlated with the ring strain in small-ring unsaturated macrocycles. Two 8-membered rings could ring-open in the presence of water, and the open forms undergo metal-template-promoted condensation to yield the 16-membered tetraaza macrocyclic complexes with a trans-diene structure. It is believed that the 18-membered macrocycle Me_6[18]diene exists as a 9-membered[8,14] (L_F) diaza ring while Me_6[22]diene does not exist as a diaza ring[9] (L_G).

Chart II



Reduction of the diene with $NaBH_4$ yields a mixture of the *C-meso* and *C-rac* isomers of Me_2[14]ane. The mixture can be resolved by fractionation from xylene, in which the *C-meso* isomer has a lower solubility. Both *C-meso-* and *C-rac*-Me_2[16]ane are quite stable, as they exist in the free state as 16-membered tetraazamacrocycles, and can be stored at ambient temperature in dark-colored bottles for several weeks without any apparent change. The infrared spectra of these isomers do not show any band around 1650 cm^{-1} assignable to $\nu_{C=N}$ and show a ν_{NH} band at 3250 cm^{-1}. The infrared spectra of the *C-meso* and *C-rac* forms show subtle differences in the 1400–800-cm^{-1} region, indicating that the two fractions are indeed different. The mass spectra of both isomers are almost identical and give m/e = 256.

Molecular models show that the *C-meso* isomer L_M should have one methyl with an axial orientation and the second methyl with an equatorial one. As compared to this, the *C-rac* isomer L_R should have both methyls equatorially oriented. It is, therefore, expected that the ^1H NMR spectra of the *C-meso* isomer should show two methyl doublets corresponding to an equatorial and an axial methyl, while the *C-rac* isomer should show a single methyl doublet for the diequatorial arrangement.[15-18] The 400-MHz ^1H NMR spectrum (Figure 1) of *C-meso*-Me_2[16]ane shows two doublets at δ 1.50 (J = 6.0 Hz) and 1.68 (J = 7.3 Hz) each corresponding to 3 protons, which can be assigned to an equatorial and an axial methyl, respectively. The spectrum of *C-rac*-Me_2[16]ane shows one doublet at δ 1.55 (J = 6.0 Hz, 6 protons) assigned to a diequatorial arrangement of the two methyls. These spectra also show two signals corresponding to 12 α-methylene protons, eight β-methylene protons, and the two coupled protons (Table II). The assignment of the signal at δ 3.90 to the coupled protons have been confirmed by double-resonance experiments. This is in accord with the 16-membered-ring structure of the two isomers.

Complexes. The ligands give blue complexes with Cu, [CuL]$(ClO_4)_2$. Conductance measurements in aqueous solutions show them to be 1:2 electrolytes. The electronic spectra of these complexes shows a single d → d band whose position is in the same region as reported for other copper(II) tetraaza macrocyclic

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Table III. Spectral and Conduction Data

compd	d → d band[a] ν, cm^{-1} (ϵ)	IR spectra, cm^{-1}				Λ, S cm^2 mol^{-1} (25 °C)
		ν_{NH}	$\nu_{C=N}$	ν_{ClO_4}	other ligand bonds	
L_M		3200				
L_R		3200				
$[CuL_D](ClO_4)_2$	17 300 (69)	3200	1620	1100, 620		171
$[NiL_D](ClO_4)_2$	21 739 sh (77)	3240	1630	1100, 610		166
$[CoL_DCl_2]ClO_4$	15 699 (56)	3220	1620	1100, 610		
$[CoL_D(NO_2)Cl]ClO_4$	20 161 (108)	3240	1630	1100, 610	1405 (asym NO_2) 810 (asym NO_2)	
$[CoL_D(NO_2)_2]ClO_4$	22 573 (87)	3200	1620	1100, 610	1410 (asym NO_2) 810 (asym NO_2)	
$[CoL_D(H_2O)_2](ClO_4)_3$	19 455 (140)	3200	1620	1100, 610		
$[CuL_M](ClO_4)_2$	16 233 (129)	3250		1100, 615		185
$[CuL_R](ClO_4)_2$	16 234 (102)	3250		1100, 615		190
$[NiL_M](ClO_4)_2$	23 094 sh (58)	3220		1100, 610		193
$[NiL_R][ClO_4]_2$	23 256 sh (90)	3200		1100, 605		185
$[CoL_MCl_2]ClO_4$	16 000 (18)[b]	3200		1100, 615		
$[CoL_RCl_2]ClO_4$	16 000 (15)[b]	3200		1100, 610		

[a] Aqueous solutions; sh = shoulder. [b] In 9 M HCl as solvent.

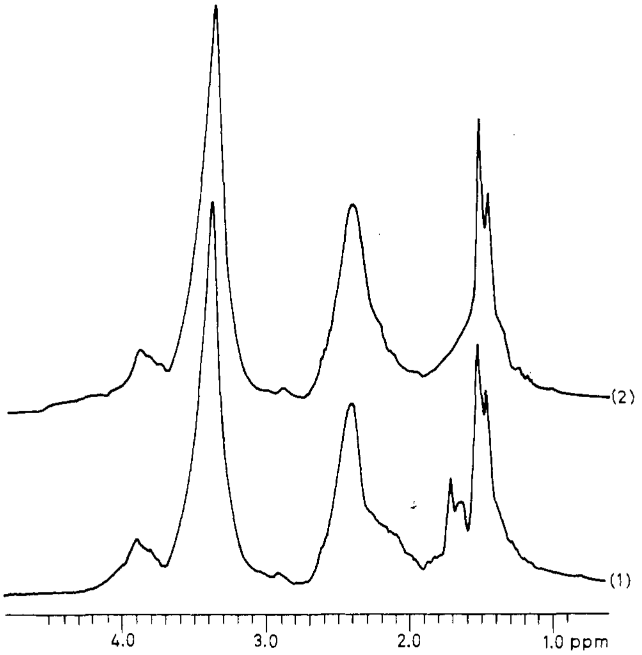

Figure 1. 400-MHz ^1H NMR spectra in trifluoroacetic acid: (1) *C-meso*-Me_2[16]ane; (2) *C-rac*-Me_2[16]ane.

complexes. The infrared spectra show the presence of characteristic ν_{NH}, $\nu_{C=N}$, and perchlorate bands (Table III). The copper(II) complexes are highly susceptible to acid-catalyzed dissociation. Their aqueous solutions rapidly become colorless on addition of 0.1 N $HClO_4$ and turn blue again on addition of an alkali.

These ligands give yellow square-planar complexes with Ni, $[NiL](ClO_4)_2$. Conductance measurements in aqueous solutions show them to be 1:2 electrolytes. Their electronic spectra show a broad shoulder in the visible region around 20 000 cm^{-1}. Their infrared spectra also show the bands expected for ν_{NH}, $\nu_{C=N}$, and ionic perchlorate (Table III). The nickel(II) complexes are also highly susceptible to acid-catalyzed dissociation.

These ligands give green octahedral complexes with Co, *trans*-$[CoLCl_2]ClO_4$, which show a d → d band around 16 500 cm^{-1}. The complexes with *C-meso*- and *C-rac*-Me_2[16]ane undergo very rapid aquation in aqueous solutions; hence, their spectra were recorded in 9 M HCl solutions. The infrared spectra of these complexes also show the characteristics ν_{NH}, $\nu_{C=N}$, and ionic perchlorate bands (Table III). *trans*-$[CoL_DCl_2]ClO_4$ undergoes axial ligand substitution to give *trans*-$[CoL_D(NO_2)Cl]ClO_4$, *trans*-$[CoL_D(NO_2)_2]ClO_4$, and *trans*-$[CoL_D(H_2O)_2]ClO_4$.

The 90-MHz ^1H NMR spectrum of $[CoL_DCl_2]ClO_4$ (Figure 2) shows a methyl signal as a singlet at δ 1.80 (6 H). The 8 β-protons appear as a singlet at δ 2.63, 12 α-protons as a singlet at δ 3.47, and the two amine protons at δ 4.50 in accord with a 16-membered-ring diene structure.

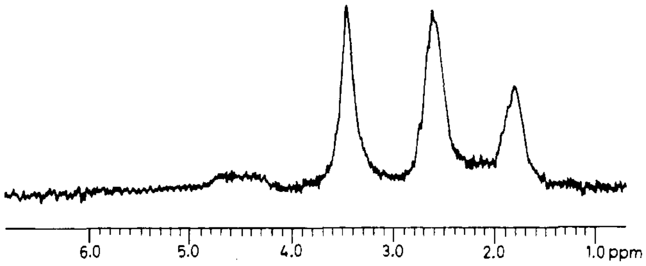

Figure 2. 90-MHz ^1H NMR spectrum of *trans*-[Co(Me_2[16]diene)-$Cl_2]ClO_4$ in $(CD_3)_2SO$.

Table IV. Kinetic Data for the Aquation of $[CoLCl_2]^+$ Complexes

L	temp, °C	10^3k_{aq}, s^{-1}	ΔH^*, kJ mol^{-1}	ΔS^*_{298}, J K^{-1} mol^{-1}	ref
L_D	9.0	8.4	84.5	+14.8	this work
	12.5	12.9			
	15.5	17.9			
	21.5	40.5			
	25.0	59.8			
[16]ane$N_4$8	25.0	3.9	47	−133	this work
	29.0	5.1			
	34.5	7.2			
	39.0	9.5			
[17]ane$N_4$9	25.0	1.5	19.6	−233	this work
	29.0	1.8			
	34.5	2.1			
	39.0	2.2			
cyclam	25.0	0.0011	103	−12	19
cyclam (X)	25.0	1.75	101.3	+42	19
isomer C	25.0	0.65	80.6	−35	18
isomer D	25.0	0.90	96.9	+22	18

Aquation Kinetics. *trans*-$[CoL_DCl_2]^+$ undergoes stepwise thermal aquation to yield $[CoL_D(H_2O)Cl]^{2+}$ in the first step and $[CoL_D(H_2O)_2]^{3+}$ in the second. Interval-scan spectra in the 33 300–25 000-cm^{-1} region show a rapid absorbance increase for the first few minutes followed by a somewhat slower absorbance decrease. The aquation of the first chloride could be followed in isolation for about 4 half-lives at 32 258 cm^{-1}. The kinetic data for the aquation of the first chloride are presented in Table IV. Comparison of the aquation data shows that *trans*-$[CoL_DCl_2]^+$ aquates at a very high rate as compared to that of other *trans*-$[CoLCl_2]^+$ complexes.

trans-$[Co(cyclam)Cl_2]^{2+}$ (with cyclam in a trans-III configuration; Chart III) aquates[19] with $k_{aq} = 0.0011 \times 10^{-3}$ s^{-1}. Large

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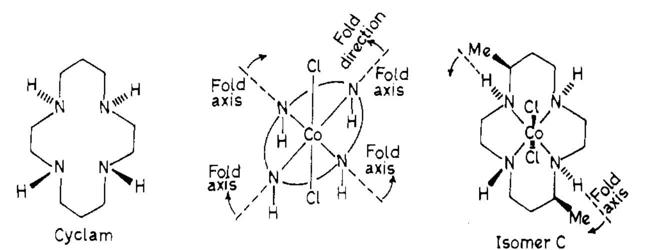
(19) Cooksey, C. J.; Tobe, M. L. *Inorg. Chem.* **1978**, *17*, 1558.

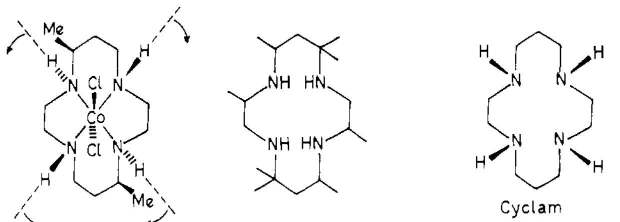
Chart III



Cyclam
trans-III form
R,S,S,R

VI

Isomer C
VII



Isomer D
VIII

Me8 [14] ane
IX

Cyclam
R,R,R,R
(S,S,S,S)
X

rate enhancements over this rate are due to steric compression exerted on the leaving group by folding of the macrocycle toward it.[20] The macrocycle can fold along a fold axis lying across two NH groups having an *N-rac* configuration (VI). The macrocycle folds away from the direction in which the NH groups lie. In the case of 13- and 14-membered rings, folding is possible only along a fold axis but larger rings can fold even against the chiral nitrogens. The high rate of aquation of *trans*-$[CoL_DCl_2]^+$ can be rationalized in terms of the ability of the macrocycle to fold. Although the aquation rates of *C-meso* and *C-rac*-Me_2[16]ane complexes could not be measured, they aquate at a much higher rate as compared to that of *trans*-$[CoL_DCl_2]^+$. This further enhancement is probably due to the availability of 2-fold axis in Me_2[16]anes. Such rate differences have been observed earlier[18] also in the case of *trans*-$[Co(C\text{-}rac\text{-}Me_2[14]ane)Cl_2]^+$ complexes, where isomer C has $k_{aq} = 0.65 \times 10^{-3}$ s^{-1} and isomer D has $k_{aq} = 0.9 \times 10^{-3}$ s^{-1}. Isomer C (VII) has a 1-fold axis while isomer D (VIII) has a 2-fold axis.

This hypothesis finds further support from the low rates of aquation of *trans*-$[Co([16]aneN_48)Cl_2]^+$ and *trans*-$[Co([17]aneN_49)Cl_2]^+$. Both of these large-ring macrocycles should be capable of folding but fail to do so due to the bulky 8- and 9-membered chelate rings. X-ray studies[21] on analogous macrocyclic complexes with 8- and 9-membered chelate rings reveal them to be highly unsymmetrical with a highly distorted skeletal structure. The already distorted structures are incapable of undergoing any kind of folding suitable for exerting steric compression on the axial sites. X-ray studies[21] have also shown that the carbon chains of the 8- and 9-membered chelate rings lie on one side of the N_4 plane. Therefore, the methylene protons adjacent to the NH groups show strong steric interaction with the axial positions on one side of the N_4 plane. This steric interaction satisfactorily accounts for the higher rate of aquation of these two complexes as compared to that of the cyclam complex. We have also prepared a series of cobalt(III) complexes of isomeric Me_8[14]anes (IX). These macrocycles are incapable of folding due to steric crowding of the eight peripheral methyl groups, and hence these isomeric complexes show low aquation rates[22] in the range of 0.5×10^{-3} s^{-1}. However, the rate enhancement over that of the cyclam complex is due to steric compression exerted by the peripheral methyl group. It has been shown that there is a good linear dependence between ln k_{aq} at 25 °C and calculated minimized conformational strain energy[20] and the strain energy increases in the order $[14]aneN_4 < [15]aneN_4 < [16]aneN_4$.

The positive value of $\Delta S^{\ddagger}$ for $[CoL_DCl_2]^+$ indicates that its aquation proceeds with a stereochemical change and should involve a trigonal-bipyramidal (D_{3h}) intermediate. A more flexible ligand geometry in the large macrocycle provides a facile distortion to the trigonal-bipyramidal state and hence a lower energy pathway to the transition state.

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Registry No. $L_D(HClO_4)_2$, 112000-23-4; L_M, 112000-24-5; L_R, 112067-02-4; $[CuL_D](ClO_4)_2$, 112000-26-7; $[NiL_D](ClO_4)_2$, 112000-28-9; *trans*-$[CoL_DCl_2]ClO_4$, 112000-30-3; *trans*-$[CoL_D(NO_2)Cl]ClO_4$, 112000-32-5; *trans*-$[CoL_D(NO_2)_2]ClO_4$, 112000-34-7; *trans*-$[CoL_D(H_2O)_2](ClO_4)_3$, 112000-36-9; $[CuL_M](ClO_4)_2$, 112000-38-1; $[CuL_R](ClO_4)_2$, 112067-04-6; $[NiL_M](ClO_4)_2$, 112000-40-5; $[NiL_R](ClO_4)_2$, 112067-06-8; *trans*-$[CoL_MCl_2]ClO_4$, 112000-42-7; *trans*-$[CoL_RCl_2]ClO_4$, 112067-94-4; *trans*-$[Co([16]aneN_48)Cl_2]ClO_4$, 92787-21-8; *trans*-$[Co([17]aneN_49)Cl_2]ClO_4$, 92787-35-4; 1,3-propanediamine, 109-76-2; methyl vinyl ketone, 78-94-4; sodium tris(carbonato)cobalt(III), 75632-02-9.

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(20) Hay, R. W.; Norman, P. R.; House, D. A.; Poon, C.-K. *Inorg. Chim. Acta* **1981**, *48*, 81.

(21) Sugimoto, M.; Fujita, J.; Ito, H.; Toriumi, K.; Ito, T. *Inorg. Chem.* **1983**, *22*, 955.

(22) Details of these studies will be published elsewhere.