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# The Preparation and Characterisation of *Cis*-Cobalt(III) Complexes of the Macrocyclic Ligands Me$_2$[14]dieneN$_4$, Me$_4$[14]dieneN$_4$, Me$_5$[14]dieneN$_4$ and Me$_6$[14]dieneN$_4$ with Chelating Ligands (acac, L-α-ala, gly, bpy, phen, ox and en)

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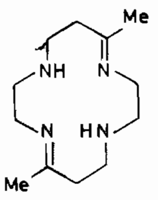
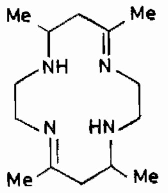
*A large number of* cis*-complexes of the type* cis*-[CoL(bidentate)]$^{n+}$ (L = Me$_2$[14]dieneN$_4$, Me$_4$[14]dieneN$_4$, Me$_5$[14]dieneN$_4$ and Me$_6$[14]dieneN$_4$; bidentate = acac, L-α-ala, gly, bpy, phen, ox and en) have been prepared and characterised. Rapid inversion of* sec-*NH centres of the macrocycle in the* trans-*[CoX$_2$(L)]$^{n+}$ complexes (X = Cl, Br) occurs in the presence of diethylamine, to give the N-*racemic *stereochemistry required in the* cis-*complexes. Infrared, electronic and $^1$H nmr spectra are reported.*

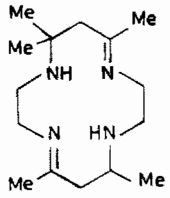
## Introduction

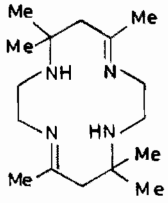
The preparation of complexes of 14-membered tetramines has been extensively studied in recent years [1]. Such ligands normally give *trans*-[CoL(X)$_2$]$^{n+}$ complexes and only in the presence of chelating ligands such as carbonate or acetylacetonate have complexes with a *cis*-geometry been reported [2–4]. The present paper describes the preparation and characterisation of a number of *cis*-complexes of the macrocyclic ligands (I–IV)[‡] with a variety of chelating ligands (acac, L-ala, gly, bpy, phen, ox and en).

## Experimental


(I) = L$_1$


(II) = L$_2$


(III) = L$_3$


(IV) = L$_4$

The various ligands were prepared as previously described, Me$_2$[14]dieneN$_4$·2HClO$_4$ [5]; Me$_4$[14]dieneN$_4$·2HClO$_4$ [4], Me$_5$[14]dieneN$_4$·2HClO$_4$ [6] and Me$_6$[14]dieneN$_4$·2HBr·2H$_2$O [7]. Previously described methods were used to prepare the *trans*-[CoCl$_2$L]$^+$ [3, 4] and the *trans*-[CoBr$_2$L]$^+$ [8] salts.

### Cis-*Complexes*

#### Cis-*[Co(Me$_2$[14]dieneN$_4$)(acac)](ClO$_4$)$_2$·propan-2-ol*

Acetylacetone (0.15 g) was added with stirring to a suspension of *trans*-[CoBr$_2$(Me$_2$[14]dieneN$_4$]-ClO$_4$ (0.54 g) in boiling methanol (30 cm$^3$). Diethylamine (*ca.* 10 drops) was added dropwise with stirring and the mixture heated on a water bath for *ca.* 5 min when the solution changed colour from green to deep red. Propan-2-ol was added until crystallisation commenced. The mixture was then cooled

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[‡] (I) = Me$_2$[14]dieneN$_4$ (5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene); (II) = Me$_4$[14]dieneN$_4$ (5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene); (III) = Me$_5$[14]diene N$_4$-(5,7,12,14,14 - pentamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene); (IV) = Me$_6$[14]diene N$_4$-(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetra-4,11-diene).

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in an ice bath and the crystals which had separated were filtered off and recrystallised by dissolving in the minimum volume of methanol and precipitating with propan-2-ol. *Anal.* Calc. for $C_{20}H_{39}Cl_2CoN_4O_{11}$: C, 37.45; H, 6.13; N, 8.74. Found: C, 36.95; H, 5.82; N, 8.88. *Cis*-$[Co(Me_4[14]dieneN_4)(acac)]ClO_4)_2$ was prepared as above. *Anal.* Calc. for $C_{19}H_{35}Cl_2CoN_4O_{10}$: C, 37.45; H, 5.79; N, 9.19. Found: C, 37.20; H, 5.61; N, 8.98%). *Cis*-$Co(Me_5[14]dieneN_4)(acac)(ClO_4)_2$ was prepared as above using both *trans*-$[CoBr_2(Me_5[14]dieneN_4]ClO_4$ and *trans*-$[CoCl_2(Me_5[14]dieneN_4)]ClO_4$. *Anal.* Calc. for $C_{20}H_{37}Cl_2CoN_4O_{10}$; C, 38.53; H, 5.98; N, 8.89. Found: C, 38.38; H, 5.92; N, 8.94 (from the chloro-complex) and C, 38.40; H, 5.94; N, 9.01% (from the bromo-complex).

### Cis-$[Co(Me_2[14]dieneN_4)(bpy)](ClO_4)_3$

A solution of 2,2′-bipyridine (0.15 g) in methanol (10 $cm^3$) was added with stirring to a suspension of *trans*-$[CoBr_2(Me_2[14]dieneN_4)]ClO_4$ (0.3 g) in boiling methanol (40 $cm^3$). A few drops of diethylamine were added and the mixture heated on a water bath for *ca.* 2 min, during which time the colour of the solution changed from green to reddish brown. The mixture was filtered hot and a solution of $LiClO_4$ (0.15 g) in methanol (10 $cm^3$) added to the filtrate. Cooling in an ice-bath gave yellow crystals which were filtered off, washed with methanol, then ether and dried *in vacuo* over silica gel. *Anal.* Calc. for $C_{22}H_{32}Cl_3CoN_6O_{12}$: C, 35.81; H, 4.37; N, 11.39. Found: C, 36.01; H, 4.03; N, 11.55%. *Cis*-$[Co(Me_4[14]dieneN_4)(bpy)](ClO_4)_3$ was prepared by a similar procedure. *Anal.* Calc. for $C_{24}H_{36}Cl_3CoN_6O_{12}$: C, 37.64; H, 4.74; N, 10.97. Found: C, 38.09; H, 4.72; N, 10.94%) as was *cis*-$[Co(Me_5[14]dieneN_4)(bpy)](ClO_4)_3$ except that *trans*-$[CoCl_2(Me_5[14]dieneN_4)]ClO_4$ was used in place of the bromo-complex. *Anal.* Calc. for $C_{25}H_{38}Cl_3CoN_6O_{12}$: C, 38.50; H, 4.91; N, 10.78. Found: C, 38.40; H, 4.83; N, 10.93%.

### Cis-$[Co(Me_6[14]dieneN_4)(bpy)](ClO_4)_3 \cdot 0.5NaClO_4$

A solution of *trans*-$[CoCl_2(Me_6[14]dieneN_4)](ClO_4)_2$ (0.28 g) in methanol (30 $cm^3$) was stirred and heated to *ca.* 60 °C with a molar equivalent of 2,2′-bipyridyl and two molar equivalents of $NaClO_4$ for 40 min. Cooling in ice gave the yellow complex (0.22 g). *Anal.* Calc. for $C_{36}H_{40}N_6Cl_3O_{12}$, $0.5NaClO_4$: C, 37.0; H, 4.8; N, 9.9; Cl, 14.7. Found: C, 36.7; H, 4.6; N, 9.6; Cl, 15.1%.

### Cis-$[Co(Me_2[14]dieneN_4)(phen)](ClO_4)_3$

To a suspension of *trans*-$[CoBr_2(Me_2[14]dieneN_4)]ClO_4$ (0.30 g) in boiling methanol (35 $cm^3$) was added with stirring, a solution of 1,10-phenanthroline (0.10 g) in methanol (10 $cm^3$). Diethylamine (8 drops) was added and the resulting mixture was heated on a water bath for *ca.* 2 min. A solution of $LiClO_4$ (0.2 g) in methanol (20 $cm^3$) was added, and the solution allowed to cool slowly. Pale yellow crystals formed and were filtered off, washed with methanol and dried *in vacuo* over silica gel. *Anal.* Calc. for $C_{24}H_{32}Cl_3CoN_6O_{12}$: C, 37.51; H, 4.23; N, 11.03. Found: C, 37.74; H, 3.99; N, 11.17%. *Cis*-$[Co(Me_4[14]dieneN_4)(phen)](ClO_4)_3$ was prepared similarly. *Anal.* Calc. for $C_{26}H_{36}Cl_3CoN_6O_{12}$: C, 39.54; H, 4.59; N, 10.64. Found: C, 38.89; H, 4.51; N, 10.79%. *Cis*-$[Co(Me_5[14]dieneN_4)(phen)](ClO_4)_3$ was also prepared by the same method. The complex crystallised as beautiful yellow plates even without the addition of $LiClO_4$. *Anal.* Calc. for $C_{27}H_{38}Cl_3CoN_6O_{12}$: C, 40.31; H, 4.76; N, 10.45. Found: C, 40.04; H, 4.65; N. 10.65%.

### Cis-$[Co(Me_2[14]dieneN_4)(en)](Br_2(ClO_4)_3$

1,2-Diaminoethane (*ca.* 6 drops) was added to a stirred suspension of *trans*-$[CoBr_2(Me_2[14]dieneN_4]ClO_4$ (0.3 g) in hot methanol (30 $cm^3$). The mixture was gently heated on a water bath for *ca.* 1 min. Shining orange crystals of the complex formed almost immediately and these were filtered off, washed with absolute ethanol, then propan-2-ol and dried *in vacuo* over silica gel. *Anal.* Calc. for $C_{14}H_{32}Br_2ClCoN_6O_4$: C, 27.90; H, 5.35; N, 13.95. Found: C, 27.60; H, 4.92; N, 13.95%. The above preparation was repeated in the presence of $LiClO_4 \cdot H_2O$ (0.1 g) but the compound again crystallised as the dibromide perchlorate (Found: C, 27.84; H, 5.44; N, 13.94%). A similar preparation using *trans*-$[CoCl_2(Me_2[14]dieneN_4)]ClO_4$ gave *cis*-$[Co(Me_2[14]dieneN_4)(en)]Cl_2(ClO_4)$. *Anal.* Calc. for $C_{14}H_{32}Cl_3CoN_6O_4$: C, 32.7; H, 6.3; N, 16.4; Cl, 20.7. Found: C, 32.5; H, 6.2; N, 16.7; Cl, 20.5%.

### Cis-$[Co(Me_4[14]dieneN_4)(en)](ClO_4)_3$

*Trans*-$[CoBr_2(Me_4[14]dieneN_4)]ClO_4$ (0.3 g) in methanol-water (30 $cm^3$, 3:1 v/v) was heated almost to boiling and 1,2-diaminoethane (8 drops) added with stirring. The resulting mixture was heated on a water bath for *ca.* 1 min and filtered hot. $LiClO_4 \cdot H_2O$ (0.1 g) in methanol (20 $cm^3$) was added and the red solution heated for *ca.* 1 min. The volume of the solution was reduced to *ca.* 5 $cm^3$ on a rotary evaporator. Addition of hot methanol (15 $cm^3$) and cooling in a refrigerator gave orange crystals. *Anal.* Calc. for $C_{16}H_{36}Cl_3CoN_6O_{12}$; C, 28,69; H, 5.42; N, 12.55. Found: C, 28.76; H, 5.51; N, 12.46%. A similar preparation using *trans*-$[CoBr_2(Me_4[14]dieneN_4)]ClO_4$ but without the addition of $LiClO_4$ gave *cis*-$[Co(Me_4[14]dieneN_4)(en)]Br_2(ClO_4)0.5H_2O$. *Anal.* Calc. for $C_{16}H_{37}Br_2ClCoN_6O_{4.5}$: C, 30.04; H, 5.83; N, 13.14. Found: C, 29.90; H, 5.48; N, 12.72%. Similar routes to the above were used to prepare *cis*-$[Co(Me_5[14]dieneN_4)(en)](ClO_4)_3 \cdot H_2O$

(which crystallises readily using the *trans*-[$CoBr_2$-L]$ClO_4$ starting material without addition of $LiClO_4$. *Anal.* Calc. for $C_{17}H_{40}Cl_3CoN_6O_{13}$: C, 29.46; H, 5.81; N, 12.12. Found: C, 29.11; H, 5.43; N, 12.59%) and *cis*-[Co($Me_6$[14]diene$N_4$(en)]($ClO_4$)$_3$ which crystallised as a yellow solid on addition of sodium perchlorate. *Anal.* Calc. for $C_{18}H_{40}Cl_3CoN_6O_{12}$: C, 31.0; H, 5.8; N, 12.0; Cl, 15.3. Found: C, 31.1; H, 5.9; N, 12.1; Cl, 15.6%.

### Cis-*[Co(Me$_2$[14]dieneN$_4$)(ox)]ClO$_4$·H$_2$O*

A solution of oxalic acid dihydrate (0.14 g) in methanol (10 cm$^3$) was added to a suspension of *trans*-[$CoBr_2$($Me_2$[14]diene$N_4$)]$ClO_4$ (0.3 g) in boiling methanol (30 cm$^3$) and the mixture heated on a water bath for *ca.* 1 min. Diethylamine was added dropwise with constant stirring until the colour of the solution changed from green to red. The reaction mixture was gently heated for *ca.* 1 min when pale red fibre-like crystals formed. These were filtered off after cooling and washed thoroughly with methanol then diethyl ether and dried *in vacuo* over silica gel. *Anal.* Calc. for $C_{14}H_{26}ClCoN_4O_9$: C, 34.40; H, 5.36; N, 11.46. Found: C, 34.16; H, 4.96; N, 11.50%. A dihydrate can also be isolated depending upon the degree of drying employed. *Cis*-[Co($Me_4$[14]diene$N_4$)(ox)]$ClO_4$, 0·5$H_2O$ was prepared similarly. *Anal.* Calc. for $C_{16}H_{31}ClCoN_4O_{9.5}$: C, 37.18; H, 5.94; N, 10.65. Found: C, 36.64; H, 5.63; N, 10.65%. *Cis*-[Co($Me_6$[14]diene$N_4$)(ox)]-$ClO_4$·$NaClO_4$·$H_2O$ was isolated in the presence of $NaClO_4$ to effect crystallisation. *Anal.* Calc. for $C_{18}H_{34}N_4O_{13}Cl_2CoNa$: C, 32.4; H, 5.1; N, 8.4; Cl, 10.6. Found: C, 31.9; H, 5.1; N, 8.4; Cl, 10.3%.

### Cis-*[Co(Me$_2$[14]dieneN$_4$)(gly)](ClO$_4$)$_2$*

Glycine (0.1 g) in methanol–water (10 cm$^3$, 6:4 v/v) was added to a stirred suspension of *trans*-[$CoBr_2$($Me_2$[14]diene$N_4$)]$ClO_4$ (0.30 g) in methanol (10 cm$^3$) and the resulting mixture heated on a water bath for *ca.* 1 min. Diethylamine (*ca.* 1 cm$^3$) was added dropwise followed by $LiClO_4$·$H_2O$ (0.15 g) and the mixture heated gently for a further 2 min. Cooling in a refrigerator overnight gave well formed red crystals. *Anal.* Calc. for $C_{14}H_{28}Cl_2CoN_5O_{10}$: C, 30.27; H, 5.08; N, 12.61. Found: C, 30.91; H, 5.22; N, 12.88%.

### Cis-*[Co(Me$_4$[14]dieneN$_4$)(gly)](ClO$_4$)$_2$·H$_2$O*

A mixture of glycine (0.10 g) and *trans*-[$CoBr_2$-($Me_4$[14]diene$N_4$)]$ClO_4$ (0.30 g) in methanol (30 cm$^3$) was heated on a water bath for *ca.* 1 min. Diethylamine (1 cm$^3$) was added dropwise with constant stirring and the mixture heated for *ca.* 1 min, filtered and the filtrate allowed to cool. Addition of $HClO_4$ (3 drops, 70%) and refrigeration for 24 hr gave red crystals which were washed with ethanol, then ether and dried *in vacuo* over silica gel. *Anal.* Calc. for $C_{16}H_{34}Cl_2CoN_5O_{11}$: C, 31.91; H, 5.69; N, 11.62. Found: C, 32.24; H, 5.56; N, 11.53%.

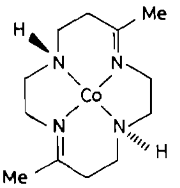
### Cis-*[Co(Me$_2$[14]dieneN$_4$)(L-α-ala)](ClO$_4$)$_2$*

A mixture of *trans*-[$CoBr_2$($Me_2$[14]diene$N_4$)]-$ClO_4$ (0.30 g) and L-α-alanine (0.05 g) in methanol (20 cm$^3$) was heated on a water bath. Diethylamine was added dropwise until the solution changed colour from green to red. A solution of $LiClO_4$·3$H_2O$ (0.10 g) in methanol (20 cm$^3$) was added and the mixture heated (*ca.* 1 min), then filtered. The filtrate was reduced in volume to *ca.* 10 cm$^3$ and then stored in a refrigerator for 48 hr to give shining needle like crystals. *Anal.* Calc. for $C_{15}H_{31}Cl_2CoN_5O_{10}$: C, 31.53; H, 5.46; N, 12.25. Found: C, 31.52; H, 5.45; N, 12.16%. *Cis*-[Co($Me_4$[14]diene$N_4$)-(L-α-ala)]($ClO_4$)$_2$ and *cis*-[Co($Me_6$[14]diene$N_4$) (L-α-ala)]($ClO_4$)$_2$·2$H_2O$ were prepared similarly. *Anal.* Calc. for $C_{17}H_{35}Cl_2CoN_5O_{10}$: C, 34.07; H, 5.89; N, 11.69. Found: C, 33.74; H, 6.12; N, 11.34. *Anal.* Calc. for $C_{19}H_{42}N_5CoO_{12}Cl_2$: C, 34.4; H, 6.4; N, 10.6; Cl, 10.7. Found: C, 34.0; H, 6.6; N, 10.3; Cl, 10.9%.

Infrared spectra were determined as KBr discs using a Perkin-Elmer 402 instrument. Electronic spectra were measured using aqueous solutions on a Perkin-Elmer 402 instrument or a Varian 635D spectrophotometer. $^1H$ nmr spectra were recorded at 60MHz on a Perkin-Elmer R10 or at 80 MHz on a Bruker WP80 spectrometer using solutions in $D_2O$ or $d_6$-DMSO.

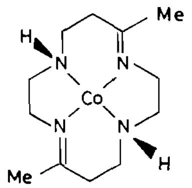
## Results and Discussion

Complexes of the various dienes have two chiral nitrogen centres. For planar coordination of the macrocycle leading to *trans*-[$CoLX_2$]$^{n+}$ complexes these two diastereoisomers are shown in (V) and (VI).



(V)

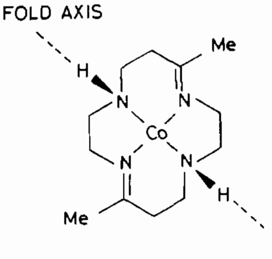
N-MESO



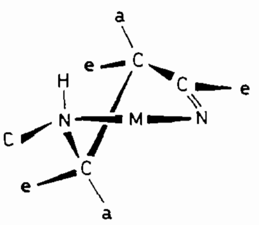
(VI)

N-RACEMIC

Previous work on *trans*-[$CoCl_2L$]$^+$ complexes derived from $Me_6$[14]diene$N_4$ [3] and $Me_2$[14]diene$N_4$ [2] have shown that the N-*meso* and N-*racemic* diastereoisomers have comparable stability. *Cis*-complexes require the [14]4,11-diene$N_4$ ligands to have the N-*racemic* configuration with the fold axis indicated in (VII). Fourteen membered rings cannot fold 'against' the secondary nitrogen donors. The [14]4,11-diene$N_4$ ligands in folded coordination have the conformation shown in (VIII) for the six-membered chelate rings (a = axial substituent; e = equatorial substituent) [1].



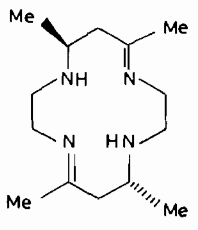
(VII)



(VIII)

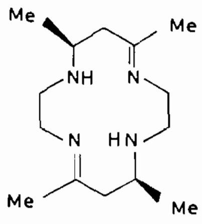
Secondary NH protons rapidly exchange in basic conditions (pH 6–7.5) and this process has been studied kinetically with a number of nickel(II) complexes of ligands of this type [9]. The four ligands employed in the present study readily fold on cobalt(III) in the presence of diethylamine which is a strong base ($pK_a = 10.93$), but a weakly coordinating ligand. The use of diethylamine allows conversion of the N-*meso* diastereoisomer to the N-*racemic* diastereoisomer required for formation of the *cis*-complex.

The ligand $Me_4$[14]diene$N_4$ contains two chiral centres at C-7 and C-14 so that C-*meso* (IX) and C-*racemic* (X) diastereoisomers can occur. Fractional crystallisation of crude [Ni($Me_4$[14]diene$N_4$]($ClO_4$)$_2$ from methanol water gives two diastereoisomers (C-*meso ca.* 80%) C-*racemic ca.* 20%) [11]. Quantitative chromatographic separations of these diastereoisomeric nickel complexes have been developed using SP-Sephadex C-25 resin and sodium glycinate as eluant [12]. X-ray crystallography of the planar nickel complexes indicates the N-*racemic* stereochemistry for the chiral nitrogen centres [13, 14]. Diastereoisomeric *cis*-complexes are thus expected with this macrocycle.



C-MESO

(IX)



C-RACEMIC

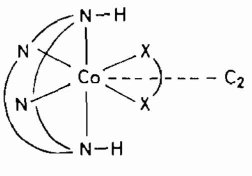
(X)

$^1H$ nmr measurements on *cis*-[Co($Me_4$[14]diene$N_4$)(acac)]($ClO_4$)$_2$ in $d_6$-DMSO indicate a methyl doublet at 1.45 $\delta$ (J *ca.* 6 Hz) with satellite signals. The methyl signal of the acetylacetonate ligand occurs as two sharp singlets at 2.05 $\delta$ and 2.14 $\delta$ indicating a mixture of diastereoisomers, and there are also two NH signals at 6.38 $\delta$ and 6.60 $\delta$. A single vinyl proton resonance occurs at 5.82 $\delta$ (acetylacetonate proton). Integration of the methyl and NH signals indicates a *ca.* 60:40 mixture of diastereoisomers. Attempts to separate the diastereoisomers on G-10 Sephadex were unsuccessful.

### *$^1H$ nmr Spectra*

Proton nmr spectra of the *cis*-complexes of $Me_2$-[14]diene$N_4$ generally display a sharp singlet at 2.48 $\delta$ from NaTMS in $D_2O$, assigned to the methyl groups attached to the imine carbon. Other multiple resonances for the ring skeleton fall in the region 2.90–4.00 $\delta$. On chelation of the unsymmetrical alanine, however, the singlet for the imine methyls is observed as two separate resonances of equal intensity at 2.45 and 2.51 $\delta$, as the methyl groups are no longer equivalent. The methyl doublet of chelated alanine is observed at 1.48 $\delta$, the ethylene protons in chelated ethylenediamine at 2.90 $\delta$, and the resonances of chelated bpy in the region 7.9 to 8.6 $\delta$. These resonances are in similar positions in complexes of $Me_6$-[14]diene$N_4$. For the latter complexes the imine methyl singlet is at 2.50 $\delta$, with resonances of equal intensity at 1.51 and 1.62 $\delta$ assigned to the geminal methyl groups of this macrocycle. Resonance positions of the macrocyle protons are not shifted appreciably upon changing the bidentate ligand.

The spectrum of *cis*-[Co($Me_2$[14]diene$N_4$)(acac)]($ClO_4$)$_2$·$(CH_3)_2CHOH$ in $d_6$-DMSO has the methyl doublet due to isopropanol at 1.06 $\delta$ (J = 7.5 Hz), the methyl singlet of $acac^-$ at 2.08 $\delta$ and the imine methyl of the macrocycle at 2.40 $\delta$. The vinyl proton of $acac^-$ occurs at 5.28 $\delta$ as a sharp singlet. A single symmetrical NH resonance occurs at 7.33 $\delta$. Complexes (of the centro symmetric ligands) containing symmetrical bidentate ligands such as $acac^-$ with the macrocycle conformation (VIII) have a $C_2$ axis as shown in (XI) and a single proton resonance is expected. The spectrum of *cis*-[Co($Me_2$-[14]diene$N_4$)(bpy)]$^{3+}$ in concentrated DCl also shows only one amine proton resonance at 7.16 $\delta$.



(XI)

### Infrared Spectra

The ir spectra of the *cis*-complexes are generally more complex than those of *trans*-complexes due to the lowered symmetry of the *cis*-derivatives. The dihydroperchlorate salts of the ligands have νCN at 1665 ($L_1$), 1670 ($L_2$) and 1660 ($L_3$) and the characteristic perchlorate bands at 1100 $cm^{-1}$ (br) and 620 $cm^{-1}$. The *cis*-acac derivatives display νCN in the region 1648–1655 $cm^{-1}$ and two bands near 1570 $cm^{-1}$ and 1520 $cm^{-1}$ due to C=C and C=O stretching vibrations of the $acac^-$ ligand. The complex *cis*-$[CoL_1(acac)](ClO_4)_2 \cdot (CH_3)_2CHOH$ has a broad νOH at 3420 $cm^{-1}$ due to the solvating alcohol.

The amino-acid derivatives have broad bands near 1650 $cm^{-1}$ assigned to the asymmetric stretching vibration of the coordinated $CO_2^-$ group; and the glycinato derivatives have the $CO_2^-$ symmetric stretching vibration in the region 1360–1370 $cm^{-1}$. The νCN vibration is obscured in the amino acid derivatives. The oxalato complexes have bands at 1707–1710 $cm^{-1}$ and 1680 $cm^{-1}$ assigned to νC=O asymmetric in bidentate oxalate. The ν(CO) symmetric band occurs near 1390 $cm^{-1}$. In $K_3[Co(ox)_3] \cdot 3H_2O$ these various bands occur at 1707, 1670 and 1398 $cm^{-1}$ [10]. The νC=N stretching vibration of the macrocyle is normally observed near 1650 $cm^{-1}$ in the complexes. All the complexes with perchlorate counter ions have the expected $ClO_4^-$ bands near 1100 $cm^{-1}$ and 620 $cm^{-1}$.

Normally a single νNH band due to the *sec* NH groups of the macrocycle can be distinguished. This band usually appears in the range 3100–3250 $cm^{-1}$, but its position can be quite variable presumably as a result of hydrogen bonding within the complex. Thus the νNH band in the $[CoL(aca)]^{2+}$ complexes occurs at 3090 $cm^{-1}$ ($L_1$), 3215 $cm^{-1}$ ($L_2$) and 3220 $cm^{-1}$ ($L_3$), and in the bpy complexes at 3210 ($L_1$), 3185 ($L_2$) and 3200 ($L_3$).

### Electronic spectra

The electronic absorption spectra of the complexes are typical of those expected for complexes with $CoN_6$, $CoN_5O$ or *cis*-$CoN_4O_2$ chromophores with two absorption bands associated with the ${}^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ and the ${}^1A_{1g} \rightarrow {}^1T_{2g}(O_h)$ transitions, Table I. All the complexes show a similar general trend in the lower energy ligand field band, with the ligand field of the macrocycle decreasing in the order $Me_2[14]dieneN_4 > Me_4[14]dieneN_4 > Me_5[14]dieneN_4 > Me_6[14]dieneN_4$. A markedly stronger ligand field is observed in all the complexes of $Me_2[14]dieneN_4$. A similar trend is also observed in the *trans*-$[CoLX_2]^{n+}$ complexes [2].

TABLE I. Electronic Spectra of the Complexes.

| Compound | $\lambda_{max}{}^c$ (nm) | $\lambda_{max}{}^c$ (nm) |
|---|---|---|
| *cis*-$[CoL_1(acac)](ClO_4)_2 \cdot (CH_3)_2CHOH$ | 487(138) | 370sh |
| *cis*-$[CoL_2(acac)](ClO_4)_2$ | 498(162) | |
| *cis*-$[CoL_3(acac)](ClO_4)_2$ | 506(152) | 360sh (*ca.* 293) |
| *cis*-$[CoL_1(bpy)](ClO_4)_3$ | 430(56) | 316(9,700) |
| *cis*-$[CoL_2(bpy)](ClO_4)_3$ | 456(52) | 318sh(8,200) |
| *cis*-$[CoL_3(bpy)](ClO_4)_3$ | 460(65) | 317sh(8,000) |
| *cis*-$[CoL_4(bpy)](ClO_4)_3O \cdot 5NaClO_4$ | 458(90) | |
| *cis*-$[CoL_1(phen)](ClO_4)_3$ | 438(50) | 348(813) |
| *cis*-$[CoL_2(phen)](ClO_4)_3$ | 450(71) | 348(819) |
| *cis*-$[CoL_3(phen)](ClO_4)_3$ | 465(93) | 348(862) |
| *cis*-$[CoL_1(en)]Br_2ClO_4$ | 466(81) | 342(83) |
| *cis*-$[CoL_2(en)](ClO_4)_3$ | 471(96) | 342(119) |
| *cis*-$[CoL_3(en)](ClO_4)_3 \cdot H_2O$ | 478(145) | 345(165) |
| *cis*-$[CoL_4(en)](ClO_4)_3$ | 474(98) | 340sh |
| *cis*-$[CoL_1(gly)](ClO_4)_2$ | 490(89) | 346(126) |
| *cis*-$[CoL_2(gly)](ClO_4)_2 \cdot H_2O$ | 490(114) | 350(126) |
| *cis*-$[CoL_1(ala)](ClO_4)_2$ | 490(103) | 348(139) |
| *cis*-$[CoL_2(ala)](ClO_4)_2$ | 496(132) | 352(157) |
| *cis*-$[CoL_4(ala)](ClO_4)_2 \cdot 2H_2O$ | 503(100) | 350(169) |
| *cis*-$[CoL_1(oX)](ClO_4) \cdot 2H_2O$ | 503(113) | 365(199) |
| *cis*-$[CoL_4(oX)](ClO_4) \cdot NaClO_4 \cdot H_2O$ | 501(120) | 368(185) |
| *cis*-$[CoL_1(CO_3)]ClO_4{}^a$ | 504(133) | 360(167) |
| *cis*-$[CoL_4(CO_3)]ClO_4{}^b$ | 500(121) | 350(135) |

$L_1 = Me_2[14]dieneN_4$; $L_2 = Me_4[14]dieneN_4$; $L_3 = Me_5[14]dieneN_4$; $L_5 = Me_6[14]dieneN_4$.

[a] R. W. Hay and G. A. Lawrance, *J. Chem. Soc. Dalton Trans.*, 1086 (1976). [b] N. Sadasivan, J. A. Kernohan and J. F. Endicott, *Inorg. Chem.*, *6*, 770 (1967). [c] The absorption coefficients ($M^{-1}$ $cm^{-1}$) are given in parentheses.

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## References

1 See for example, 'Coordination Chemistry of Macrocyclic Compounds', ed. G. A. Melson, Plenum Press, New York, N.Y., 1979.
2 R. W. Hay and G. A. Lawrance, *J. Chem. Soc. Dalton Trans.*, 1466 (1975).
3 N. Sadasivan, J. A. Kernohan and J. F. Endicott, *Inorg. Chem.*, *6*, 770 (1967).
4 R. W. Hay and B. Jeragh, *J. Chem. Soc. Dalton,* 1261 (1977).
5 R. A. Kolinski and B. Korybut-Daszkiewicz, *Bull. Acad. Pol. Sci.*, *17*, 13 (1969).
6 R. W. Hay and M. A. Ali, in preparation.
7 R. W. Hay, G. A. Lawrance and N. F. Curtis, *J. Chem. Soc. (Perkin I)*, 591 (1975).
8 R. W. Hay and M. A. Ali, in preparation.
9 E. Sledziewska, *Bull. Acad. Pol. Sci.*, *20*, 49 (1972).
10 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds', 3rd ed., Wiley New York, 1978, p. 234.
11 R. A. Kolinski and B. Korybut-Daskiewicz, *Inorg. Chim. Acta*, *14*, 237 (1975).
12 G. H. Searle, R. W. Hay and B. Jeragh, *Aust. J. Chem.*, *33*, 1447 (1980).
13 A. I. Gusiev, J. W. Krayewski and Z. Urbanczyk, *Bull. Acad. Pol. Sci.*, *22*, 387 (1974).
14 J. W. Krajewski, Z. Urbanczyk-Lipkowka and P. Gluzinski, *Bull. Acad. Pol. Sci.*, *22*, 955 (1974).