Transition-metal Complexes of the Macrocyclic Ligand 5,7,12,14-Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene

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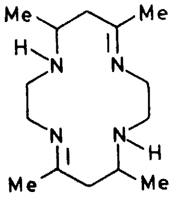
The reaction of the monohydroperchlorate salt of 1,2-diaminoethane with pent-3-en-2-one in methanol solution gives the dihydroperchlorate salt of 5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (L·2HClO$_4$). The reaction is not completely stereospecific and *ca.* 15% of the C-*rac*-ligand is formed in conjunction with the C-*meso*-ligand. A series of octahedral cobalt(III) complexes of the general type *trans*-[CoLX$_2$]$^{n+}$ (X = Cl$^-$, Br$^-$, [NO$_2$]$^-$, [CN]$^-$, [N$_3$]$^-$, [MeCO$_2$]$^-$, NH$_3$, or Cl$^-$-[NO$_2$]$^-$) have been prepared by anion-metathesis reactions with the C-*meso*-N-*meso* (e–e) stereoisomer of *trans*-[CoCl$_2$L]$^+$, and n.m.r. studies confirm this configuration in the other complexes. The preparations of the μ-peroxo-complex [{CoL(OH$_2$)}$_2$O$_2$][ClO$_4$]$_4$·H$_2$O and the four-coordinate complex [CuL][ClO$_4$]$_2$ are also described. The stereochemistry of the various complexes is discussed and i.r. and *d–d* spectra are reported.

THE reaction of the monohydroperchlorate salt of 1,2-diaminoethane with pent-3-en-2-one in methanol solution gives the dihydroperchlorate salt of the macrocyclic ligand 5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (L). The ligand contains two chiral carbon centres at C^7 and C^{14} so that C-*rac* (I) and

C-*meso* (II) diastereoisomers of the ligand can occur. Kolinski and Korybut-Daszkiewicz[1] studied the nickel(II) complexes of the ligand in detail. Fractional crystallisation of the crude [NiL][ClO_4]$_2$ complex from 90% methanol gave two isomers, A (orange crystals, least soluble) and B (yellow needles). The ratio of isomer A to B was *ca.* 5 : 1. Isomer A was considered to be a derivative of the C-*meso*-ligand and B of the C-*rac*-ligand. This conclusion has subsequently been confirmed by *X*-ray crystallography.[2,3,] *



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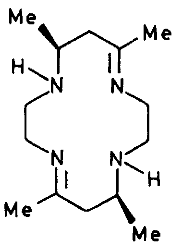
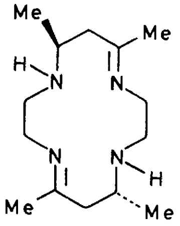


(I) C-*rac*



(II) C-*meso*

The present paper discusses further aspects of the coordination chemistry of the ligand with particular emphasis on the cobalt(III) derivatives.

EXPERIMENTAL

5,7,12,14-*Tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene Dihydroperchlorate*.—The ligand was prepared as follows. Perchloric acid (41.5 cm^3 of 72%, 0.5 mol) was added dropwise with continuous stirring to a cooled (ice–salt bath) solution of 1,2-diaminoethane (33.5 cm^3, 0.5 mol) dissolved in methanol (350 cm^3). On completion of the addition the reaction mixture was cooled to −5 °C. Pent-3-en-2-one (40.5 cm^3, 0.5 mol) diluted with an equal volume of methanol was then added dropwise with continuous stirring, the temperature being maintained between 0 and 5 °C. On completion of the addition the mixture was stirred for 4 h during which time the temperature was allowed to increase to ambient. The resulting suspension was stored overnight in a refrigerator. The white *product* was filtered off, washed thoroughly with methanol, then diethyl ether, and dried *in vacuo*, yield *ca.* 60 g, m.p. 120—123 °C (Found: C, 37.4; H, 6.7; N, 12.2. Calc. for $C_{14}H_{28}N_4 \cdot 2HClO_4$: C, 37.1; H, 6.7; N, 12.35%).

(5,7,12,14-*Tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*nickel*(II) *Perchlorate*.—This complex was prepared essentially as described previously.[1] It was fractionally crystallised from hot water. The first fractions gave the orange isomer [Aα = N-*rac*-C-*meso* (a–e)] and subsequent fractional recrystallisation gave small amounts of the yellow isomer [Bβ = N-*rac*-C-*rac* (a–a)] [Found: C, 31.8; H, 5.7; N, 10.4. $C_{14}H_{28}Cl_2N_4NiO_8 \cdot H_2O$ (orange isomer) requires C, 31.95; H, 5.4; N, 10.65%. Found: C, 33.2; H, 5.7; N, 10.85. $C_{14}H_{28}Cl_2N_4NiO_8$ (yellow isomer) requires C, 32.95; H, 5.6; N, 11.0%].

(5,7,12,14-*Tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*copper*(II) *Perchlorate*.—Copper(II) carbonate (0.7 g) was suspended in water (30 cm^3) and a slight excess of the ligand dihydroperchlorate (1 g) was added. The mixture was heated on a water-bath for 30 min. The red-purple solution was filtered while hot and the filtrate was evaporated to dryness on a rotary evaporator. The resulting solid was dissolved in the minimum volume of hot methanol. Cooling in ice gave reddish purple crystals, which were filtered off, washed with ice-cold methanol then diethyl ether, and finally dried *in vacuo* (Found: C, 32.4; H, 5.2; N, 11.0. $C_{14}H_{28}Cl_2CuN_4O_8$ requires C, 32.65; H, 5.5; N, 10.9%).

trans-*Dichloro*(5,7,12,14-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate*.—This complex was prepared by two different routes. (*a*) A slurry of sodium tris(carbonato)cobaltate(III) trihydrate (0.8 g) and the ligand dihydroperchlorate (0.8 g) was prepared in methanol–water (30 cm^3, 1 : 1 v/v) and heated on a water-bath until effervescence ceased (*ca.* 20 min). The resulting red solution was filtered while hot and concentrated hydrochloric acid (15 cm^3) was added to the filtrate. The volume was reduced on a water-bath and on cooling shiny green crystals were obtained. The *product* was filtered off and recrystallised from hot methanol (Found: C, 35.2; H, 6.0; N, 11.5. $C_{14}H_{28}Cl_3CoN_4O_4$ requires C, 34.9; H, 5.85; N, 11.6%).

(*b*) A hot solution of cobalt(II) acetate tetrahydrate (2.5 g, 0.01 mol) in methanol (100 cm^3) was added to the ligand dihydroperchlorate (4.5 g, 0.01 mol). The mixture was heated on a water-bath for 30 min, filtered while hot, and then cooled. The filtrate was diluted with methanol–water (100 cm^3, 1 : 1 v/v) and air was passed through the solution for *ca.* 20 h. The methanol was removed on a rotary evaporator and concentrated HCl (40 cm^3) was added to the dull red solution. The green *product* was isolated by slow evaporation on a steam-bath followed by cooling in an ice-bath, and was recrystallised from *ca.* 6 mol dm^{-3} HCl (Found: C, 34.7; H, 5.7; N, 11.8. $C_{14}H_{28}Cl_3CoN_4O_8$ requires C, 34.9; H, 5.85; N, 11.6%). The complex prepared by (*b*) is less soluble in 0.1 mol dm^{-3} HCl than that prepared by (*a*). N.m.r. work (see later) confirmed that the isomer from (*b*) is a pure stereoisomer and for this reason this material was used for the subsequent preparations.

trans-*Dibromo*(5,7,12,14-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate*.—A solution of *trans*-[$CoCl_2L$][ClO_4] (0.2 g) in a 10% methanolic solution of hydrobromic acid (25 cm^3) was evaporated to a small volume (*ca.* 3 cm^3) on a steam-bath. The apple-green

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* *Note added in proof*: The *X*-ray data on these complexes are rather ambiguous as the two isomers are not clearly defined. The crystal structure discussed in ref. 2 is that of the minor yellow isomer (C-*rac*-ligand) *i.e.* compound VIIBα of ref. 1. The crystal structure described in ref. 3 is that of the main orange isomer (C-*meso*-ligand) *i.e.* compound VIIAα of ref. 1 (R. A. Kolinski, personal communication).

[1] R. A. Kolinski and B. Korybut-Daszkiewicz, *Inorg. Chim. Acta*, 1975, **14**, 237.

[2] J. Krajewski, Z. Urbańczyk-Lipkowska, and P. Gluzinski, *Bull. Acad. polon. Sci., Sér. Sci. chim.*, 1974, **22**, 955.

[3] A. I. Gusiev, J. W. Krajewski, and Z. Urbańczyk, *Bull. Acad. polon. Sci., Sér. Sci. chim.*, 1974, **22**, 387.

product was isolated by cooling the mixture in an ice-bath; it was recrystallised from hot methanol, washed with ice-cold methanol then diethyl ether, and dried *in vacuo* (Found: C, 29.7; H, 5.1; N, 9.7. $C_{14}H_{28}Br_2ClCoN_4O_4$ requires C, 29.5; H, 4.9; N, 9.8%).

trans-*Dinitro*(5,7,12,14-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate*.—A solution of *trans*-$[CoCl_2L][ClO_4]$ in methanol (40 cm^3) was heated with a slight excess of sodium nitrite (0.06 g) on a water-bath for 20 min. The brown solution was filtered hot and the filtrate was cooled in an ice-bath. The *product* crystallised as orange crystals which were filtered off, washed with ice-cold methanol then diethyl ether, and dried *in vacuo* (Found: C, 33.5; H, 5.7; N, 16.75. $C_{14}H_{28}ClCoN_6O_8$ requires C, 33.3; H, 5.6; N, 16.7%).

trans-*Chloronitro*(5,7,12,14-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate*.—The complex *trans*-$[CoCl_2L][ClO_4]$ [prepared by method (*a*)] (0.4 g) in hot 95% methanol (100 cm^3) was stirred with 1 mol equiv. (0.069 g) of sodium nitrite. After heating for *ca.* 20 min, the red-brown solution was filtered while hot and the filtrate was cooled in an ice-bath. The resulting fine red-brown *product* was filtered off and recrystallised from methanol. The complex was washed with methanol then diethyl ether and dried *in vacuo* (Found: C, 34.2; H, 5.8; N, 14.2. $C_{14}H_{28}Cl_2CoN_5O_6$ requires C, 34.15; H, 5.7; N, 14.2%).

trans-*Dicyano*(5,7,12,14-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate Hemihydrate*.—To a solution of *trans*-$[CoCl_2L][ClO_4]$ (0.25 g) in hot aqueous methanol was added an excess of sodium cyanide (0.8 g). The green solution immediately became yellow. The mixture was heated on a water-bath for *ca.* 30 min. The solution was concentrated until crystals appeared and was then cooled in an ice-bath. The yellow crystals of the product were filtered off, washed with cold methanol then diethyl ether, and dried *in vacuo* (Found: C, 40.7; H, 5.9; N, 18.1. $C_{16}H_{28}ClCoN_6O_4 \cdot 0.5H_2O$ requires C, 40.7; H, 5.9; N, 17.8%).

trans-*Diammine*(5,7,12,14-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Dichloride Perchlorate*. $[Co(NH_3)_2L][ClO_4]Cl_2$.—A solution of *trans*-$[CoCl_2L][ClO_4]$ (1 g) in methanol (50 cm^3) was stirred at *ca.* 55 °C and concentrated aqueous ammonia (2 cm^3, s.g. 0.88) was added. The solution became brown and then concentrated HCl was added dropwise until the solution was just acid to litmus. Additional ammonia (3 cm^3, s.g. 0.88) was then added and the yellow suspension which formed was cooled in an ice-bath for *ca.* 1 h. The yellow *product* was filtered off and recrystallised from hot water to give the mixed chloride–perchlorate salt (Found: C, 32.7; H, 6.7; N, 16.2. $C_{14}H_{34}Cl_3CoN_6O_4$ requires C, 32.6; H, 6.6; N, 16.3%).

trans-*Diacetato*(5,7,12,14-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate Dihydrate*.—To a solution of *trans*-$[CoCl_2L][ClO_4]$ (1.0 g) in hot methanol (20 cm^3) was added sodium acetate (0.75 g) followed by a few drops of glacial acetic acid. The reaction mixture was warmed on a water-bath for *ca.* 0.5 h. On cooling, pink crystals of the *product* formed. The complex was filtered off and recrystallised from hot aqueous methanol and dried *in vacuo* (Found: C, 38.05; H, 6.0; N, 9.9. $C_{18}H_{38}ClCoN_4O_{10}$ requires C, 38.25; H, 6.4; N, 9.9%).

trans-*Diazido*(5,7,12,14-*tetramethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate*.—The complex *trans*-$[CoCl_2L][ClO_4]$ (0.4 g) was dissolved in water (20 cm^3) and sodium azide (0.7 g) was added. The colour of the solution immediately became blue-violet. The reaction mixture was warmed on a water-bath for *ca.* 20 min. On cooling, shiny blue-violet crystals of the *product* were obtained. These were filtered off, washed with ethanol then diethyl ether, and dried *in vacuo* (Found: C, 34.0; H, 5.7; N, 28.3. $C_{14}H_{28}ClCoN_{10}O_4$ requires C, 34.0; H, 5.7; N, 28.3%).

trans-$[\{CoL(OH_2)\}_2O_2][ClO_4]_4 \cdot H_2O$.—The ligand dihydroperchlorate (4.5 g) was dissolved in the minimum volume of water and the solution was slowly added with continuous stirring to a concentrated aqueous solution of cobalt(II) perchlorate hexahydrate (3.6 g, 1 : 1 mol ratio). On stirring the solution rapidly became deep brown. Addition of concentrated sodium perchlorate solution (3 cm^3) and subsequent cooling in an ice-bath gave the brown *product* which was filtered off, washed with ethanol then diethyl ether, and finally dried *in vacuo* (Found: C, 30.5; H, 5.55; N, 10.1. $C_{28}H_{62}Cl_4Co_2N_8O_{21}$ requires C, 30.4; H, 5.65; N, 10.1%).

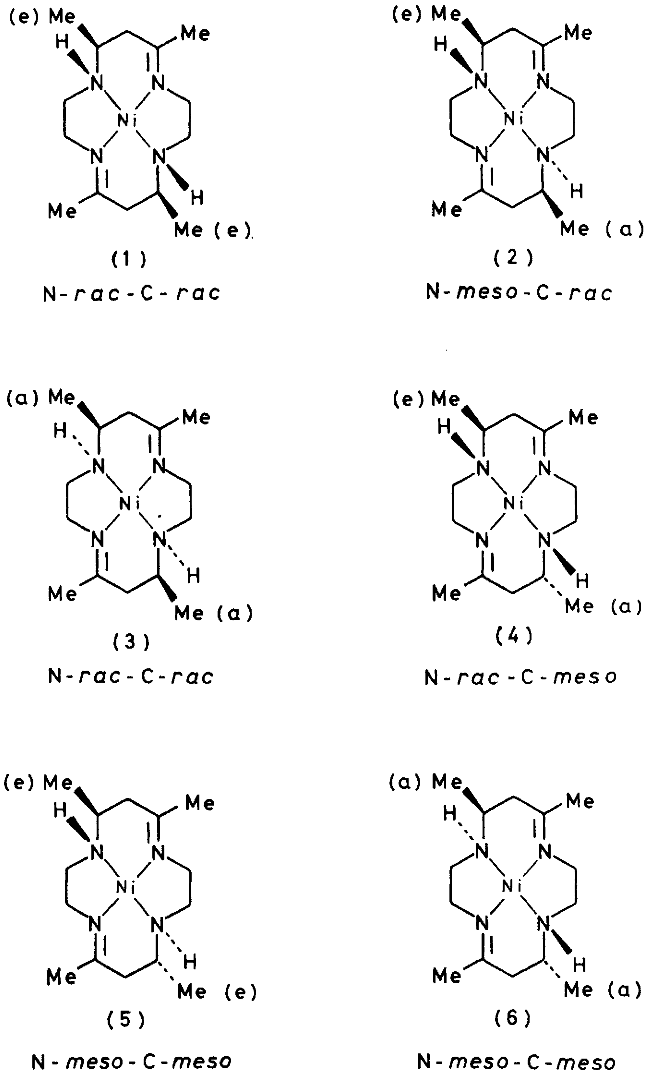
Infrared spectra were determined as KBr discs using a Perkin-Elmer 457 spectrophotometer. Visible-spectral measurements were made using a Perkin-Elmer 402 instrument with the appropriate solvent as blank. Proton n.m.r. spectra were determined using a Perkin-Elmer R34 instrument at 90 or 60 MHz with $[^2H_6]$dimethyl sulphoxide ($[^2H_6]$dmso) or CD_3NO_2 as solvent and tetramethylsilane as internal standard. Conductivity measurements were carried out at 25 °C using aqueous solutions and a Portland model P310 conductivity meter. The concentrations used were 10^{-3} mol dm^{-3}.

RESULTS AND DISCUSSION

Metal complexes of the ligand L contain two chiral nitrogen centres so that including the chiral carbon centres there is a possibility of 10 stereoisomers, *i.e.* two all-*meso* forms and four *rac* mixtures. The various stereoisomers belong to two sets, one derived from the C-*rac*-ligand and the other from the C-*meso*-ligand. The various possible diastereoisomers are shown diagrammatically in the Scheme. The complexes of one C configuration are not convertible into complexes of the other C configuration, whereas the N configurations are readily isomerised by base.

Kolinski and Korybut-Daszkiewicz[1] isolated, and characterised by n.m.r. spectra, the following nickel(II) complexes: N-*rac*-C-*rac*[Bβ(e–e)], N-*meso*-C-*rac*[Bγ(a–e)], N-*rac*-C-*rac*[Bα(a–a)], N-*rac*-C-*meso*[Aα(a–e)], and N-*meso*-C-*meso*[Aβ(e–e)]. Crystallography has subsequently been carried out on the N-*rac*-C-*rac* stereoisomer (3)[2] and on the N-*rac*-C-*meso* stereoisomer (4).[3] The former complex has both methyl groups axial, and the latter has one axial and one equatorial methyl group.

Cobalt(III) *Complexes*.—Green *trans*-$[CoCl_2L][ClO_4]$ was prepared by two routes: reaction of the ligand dihydroperchlorate with sodium tris(carbonato)cobaltate(III); and aerial oxidation of a solution of cobalt(II) acetate and the ligand dihydroperchlorate. The former reaction may proceed *via* a folded *cis*-carbonato-species and in some cases gives complexes which have a different chiral nitrogen configuration to that obtained by aerial oxidation.[4] The n.m.r. spectrum of the complex prepared by the aerial-oxidation route has a single methyl doublet at δ 1.46 p.p.m. (J 7 Hz) due to coupling with the *single ring* proton on C^7 and C^{14}. The imine methyl group occurs as a sharp singlet at 2.51 p.p.m. It has been shown [1] that in the nickel(II) complexes the axial methyl groups occur as a doublet at *ca.* 1.2—1.3 p.p.m. There is evidence that the order of assignment of the methyl resonances of cobalt(III) relative to nickel(II) complexes is reversed, with the axial substituent at higher field.[5] Thus for N-*rac*-$[NiL'][ClO_4]_2$ the equatorial methyl group occurs at 1.35 p.p.m. and the axial methyl at 2.16 p.p.m., while for the complex *trans*-N-*meso*-$[CoCl_2L'][ClO_4]$ and the corresponding N-*rac* derivative the equatorial methyl occurs at 1.68 p.p.m. and the axial methyl at 1.37 p.p.m. (L′ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene).



(1) N-*rac*-C-*rac*

(2) N-*meso*-C-*rac*

(3) N-*rac*-C-*rac*

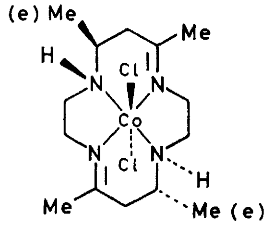
(4) N-*rac*-C-*meso*

(5) N-*meso*-C-*meso*

(6) N-*meso*-C-*meso*

SCHEME Stereoisomers of nickel(II) complexes of 5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene. (a) and (e) refer to axial and equatorial substituents respectively.

The complex *trans*-$[CoCl_2L][ClO_4]$ prepared by the carbonato-route has a more complex n.m.r. spectrum than that prepared by aerial oxidation. The former complex has a methyl doublet at 1.2 p.p.m. and two overlapping methyl doublets at *ca.* 1.5 p.p.m.; a complex pattern of methyl imine signals occurs at *ca.* 2.5 p.p.m. In view of the previous work on the n.m.r. spectra of cobalt(III) complexes of macrocyclic dienes it seems reasonable to assign the signals at *ca.* 1.2 p.p.m. to axial methyl groups and the lower-field signal at *ca.* 1.5 p.p.m. to equatorial methyl groups. Thus the n.m.r. data are consistent with the view that the complex prepared by aerial oxidation is a pure stereoisomer with both methyl groups equatorial. Since the complex is prepared from the ligand which is predominantly the C-*meso* diastereoisomer, the complex must be the N-*meso*-C-*meso* stereoisomer (III) in which both substituents are equatorial. The complex prepared by the carbonato-route is clearly a mixture of stereoisomers and the n.m.r. data could be rationalised in terms of a *ca.* 7 : 3 mixture of an (e–a) and an (e–e) set of stereoisomers.



(III)

Treating the *trans*-$[CoCl_2L][ClO_4]$ (prepared by aerial oxidation) with ammonia followed by concentrated HCl and evaporation to dryness to regenerate the *trans*-dichloro-complex gave a complex which had an identical n.m.r. spectrum to that of the starting material, *i.e.* 1.45 (d) (J 7.2 Hz) and imine methyl at 2.51 (s) p.p.m. As there is no evidence for isomerisation of the chiral centres under basic conditions, the N-*meso*-C-*meso* diastereoisomer (III) appears to be the most thermodynamically stable.

TABLE 1

N.m.r. data at 90 MHz in $[^2H_6]$dmso

	δ/p.p.m. (J/Hz)	
Complex	C-Me	imine-Me
trans-$[CoCl_2L][ClO_4]$	1.46 (d) (7.2)	2.51 (s)
trans-$[CoBr_2L][ClO_4]$	1.46 (d) (7)	2.49 (s)
trans-$[CoL(NO_2)_2][ClO_4]$	1.40 (d) (7)	2.46 (s)
trans-$[CoL(N_3)_2][ClO_4]$	1.42 (d) (7)	2.50 (s)
trans-$[CoL(O_2CMe)_2][ClO_4]\cdot 2H_2O$ *	1.52 (d) (7)	2.51 (s)
trans-$[CoL(CN)_2][ClO_4]\cdot 0.5H_2O$	1.30 (d) (7)	2.36 (s)

* The $[MeCO_2]^-$ methyl signal occurs as a singlet at 1.60 p.p.m.; d = doublet, s = singlet.

The diastereoisomer prepared by aerial oxidation was

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[4] R. W. Hay and G. A. Lawrance, *J.C.S. Dalton*, 1975, 1466.

[5] See, for example, N. F. Curtis, *Austral. J. Chem.*, 1974, **27**, 71; E. S. Gore, J. C. Dabrowiak, and D. H. Busch, *J.C.S. Chem. Comm.*, 1972, 922.

used for the subsequent preparations of the cobalt(III) complexes by anion-metathesis reactions in methanol or methanol–water solutions. Since attempts to isomerise the diequatorial complex with base were unsuccessful the N-*meso*-C-*meso* configuration of the *trans*-dichloro-complex is expected to be retained in the other complexes and this view is supported by the n.m.r. data (Table 1). With the exception of the dicyano-derivative, all the complexes have a C-methyl signal in the range 1.4—1.5 p.p.m. and a methyl imine signal at *ca.* 2.5 p.p.m. in [$^2H_6$]dmso solution. Ball and Endicott[6] observed that the chemical shifts of the imine and ring methyls in cobalt(III) complexes of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene are dependent on the axial ligand X, and in the present case quite marked shifts are observed with the *trans*-dicyano-complex.

TABLE 2

Complex	Electronic spectra [a] *d–d*	Charge transfer
$[CuL][ClO_4]_2$	520 (86)	245 (5.0 × 10^3)
$[NiL][ClO_4]_2$ (orange) [b]	442 (80)	282 (2.15 × 10^4)
trans-$[CoCl_2L][ClO_4]$ [c]	620 (32), 460 (sh) (27), 395 (sh) (67)	288 (1 × 10^4)
trans-$[CoClL(NO_2)][ClO_4]$	510 (104)	360 (4 × 10^3), 284 (1.56 × 10^4)
trans-$[CoBr_2L][ClO_4]\cdot H_2O$ [c]	660 (72), 375 (sh) (7 × 10^3)	290 (6.5 × 10^4)
trans-$[CoL(NO_2)_2][ClO_4]$	450 (202), 360 (6 × 10^3)	260 (3.3 × 10^4), 215 (3.7 × 10^4)
trans-$[Co(CN)_2L][ClO_4]\cdot 0.5H_2O$	418 (80), 335 (sh) (70)	225 (3.7 × 10^4)
trans-$[CoL(N_3)_2][ClO_4]$	564 (375), 345 (1.4 × 10^4)	220 (2.7 × 10^4)
trans-$[CoL(NH_3)_2][ClO_4]Cl_2$	458 (74), 340 (92)	220 (6.3 × 10^4)
trans-$[CoL(O_2CMe)_2][ClO_4]\cdot 2H_2O$	560 (44), 434 (38), 365 (102)	250 (2.7 × 10^4)

[a] Determined using aqueous solutions unless otherwise stated; $\lambda_{max.}$ in nm, ε in dm^3 mol^{-1} cm^{-1} in parentheses. [b] N-*rac*-C-*meso* diastereoisomer. [c] In dry acetonitrile solution.

TABLE 3

Prominent i.r. absorption bands (cm^{-1})

Compound	ν(CN)	ν(NH)	$\nu(ClO_4^-)$	Other ligand bands
$L\cdot 2HClO_4$	1 669s	3 170s	1 100vs, br, 620s	
$[NiL][ClO_4]_2$ (orange)	1 645s	3 190s	1 100vs, br, 620s	
$[CuL][ClO_4]_2$	1 665s	3 230s, 3 120s	1 100vs, br, 630s	
trans-$[CoCl_2L][ClO_4]$	1 660s	3 200s	1 100vs, br, 620s	
trans-$[CoBr_2L][ClO_4]\cdot H_2O$	1 650s	3 180m	1 090vs, br, 620s	ν(OH) 3 400m, br
trans-$[CoL(NO_2)_2][ClO_4]$	1 660s	3 160s	1 090vs, br, 620s	$\nu_{asym}(NO_2)$ 1 390s δ(ONO) 822sp, s
trans-$[Co(CN)_2L][ClO_4]\cdot 0.5H_2O$	1 660s	3 140s	1 090vs, br, 620s	ν(OH) 3 440m, br ν(CN) (co-ord.) 2 139sp, m
trans-$[CoL(N_3)_2][ClO_4]$	1 655s	3 170s	1 100vs, br, 622s	$\nu(N_3)$ (co-ord.) 2 005vs
trans-$[CoL(NH_3)_2][ClO_4]Cl_2$	1 655s	3 300s, 3 120 (sh), s, 3 060s	1 090vs, br, 622s	
trans-$[CoL(O_2CMe)_2][ClO_4]\cdot 2H_2O$	1 665s	3 070w	1 090vs, br, 622s	$\nu(O_2CMe)$ (co-ord.) 1 570vs ν(OH) 3 450m, br

vs = Very strong, s = strong, m = medium, br = broad, sp = sharp, and w = weak.

The complexes *trans*-$[CoN_4X_2]^{n+}$ have a basic D_{4h} symmetry with the $^1A_{1g}\rightarrow{}^1T_{1g}(O_h)$ splitting into two components, $^1A_{1g}\rightarrow{}^1E_{1g}(D_{4h})$ and $^1A_{1g}\rightarrow{}^1A_{2g}(D_{4h})$.[7,8] Where the tetragonal splitting is not very large (where X and N do not differ greatly in the spectrochemical series) only a single absorption band is observed under the $^1A_{1g}\rightarrow{}^1T_{1g}(O_h)$ envelope. The energies and intensities observed in the *d–d* spectra (Table 2) support the assignment of a *trans* configuration to the various complexes. In addition the i.r. spectra of the complexes in the 750—1 500 cm^{-1} region are very similar when due allowances are made for anion absorption. Folding of the ligand to give a *cis* complex leads to marked changes in the i.r. spectrum in the 750—1 500 cm^{-1} region.[4] The prominent i.r. bands of the various complexes are listed in Table 3. All the complexes have a strong ν(NH) at *ca.* 3 200 cm^{-1}. Strong bands due to ionic perchlorate occur at 1 100 and 625 cm^{-1}.

μ-Peroxo-complexes.—A few examples of peroxo-bridged cobalt(III) complexes of macrocyclic tetra-aza ligands have been reported[9,10] and the spectra of some of these complexes have been studied in detail.[11] The μ-peroxo-derivatives of macrocyclic cobalt(III) complexes are relatively easy to prepare and are more stable than

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those derived from non-cyclic ligands. Thus brown *trans*-$[\{CoL(OH_2)\}_2O_2][ClO_4]\cdot H_2O$ was readily isolated by stirring the ligand dihydroperchlorate with cobalt(II) perchlorate in aqueous solution. Addition of $Na[ClO_4]$ and cooling gave the crystalline complex which has ν(NH) at 3 200 cm^{-1}, ν(CN) at 1 655 cm^{-1}, and strong perchlorate (ionic) bands at 1 100br and 625 cm^{-1}. A broad band due to ν(OH) occurs at 3 450 cm^{-1}. Attempts to substitute the aqua-ligands with other ligands such as Cl^-, Br^-, and $[NO_2]^-$ were not completely successful.

The electronic spectra of μ-peroxo-dicobalt(III) complexes are generally poorly resolved owing to the presence of very broad charge-transfer bands in the near-u.v. region.[12] The lowest-energy ligand-field band of $[(H_3N)_5CoO_2Co(NH_3)_5]^{4+}$, for example, appears as an ill defined shoulder at *ca.* 450 nm.[11] The electronic spectra of some μ-peroxo-complexes are listed in Table 4. All the complexes have an intense charge-transfer band at *ca.* 220 nm. The derivatives of 5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene have a single charge-transfer band in the 320—340 nm region. The position and intensity of this band is a function of the $[O_2]^{2-}$ dihedral angle[11] and its assignment has been discussed in detail.[11] The complex *trans*-$[\{CoL(OH_2)\}_2O_2]^{4+}$ has a band at 535 nm which is presumably the $^1A_{1g}\rightarrow{}^1T_{1g}(O_h)$ transition. Decreasing *Dq* values of the axial groups according to $NH_3 > [NCS]^- > [O_2]^{2-} > OH_2$ have been reported.[11] For the *trans*-$[CoL(NCS)_2]^+$ chromophore the $^1A_{1g}\rightarrow{}^1T_{1g}(O_h)$ band occurs at 520 and at 575 nm for the *trans*-$[CoL(OH_2)_2]^{3+}$ chromophore, lending support to the assignment. It appears that the steric effects of the additional methyl groups may substantially reduce the intensity of the lower-energy charge-transfer transitions by modifying the $[O_2]^{2-}$ dihedral angle.

TABLE 4

Electronic spectra of μ-peroxo-complexes

Complex [a]	$\lambda_{max.}$/nm	ε/dm³ mol⁻¹ cm⁻¹
trans-$[\{CoL''(OH_2)\}_2O_2][ClO_4]_4\cdot H_2O$ [b]	460 (sh),	330,
	320 (sh),	3 870,
	218	45 500
trans-$[\{CoL(OH_2)\}_2O_2][ClO_4]_4\cdot H_2O$	535,	70,
	400 (sh),	195,
	350 (sh),	265,
	222	*ca.* 10^5

[a] L″ = 5,12-Dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene. Spectra determined in aqueous solution. [b] Prepared as described in ref. 10.

Decomposition of the bridged binuclear complexes to mononuclear cobalt(III) species is observed in acid solution. Thus heating *trans*-$[\{CoL(OH_2)\}_2O_2][ClO_4]_4\cdot H_2O$ with 6 mol dm^{-3} $HClO_4$ gives a product [$\lambda_{max.}$ 575, 430, and 370 nm (sh)] which is identical to the *trans*-diaqua-complex, $[CoL(OH_2)_2]^{3+}$, prepared by base hydrolysis of *trans*-$[CoCl_2L]^+$ followed by acidification with $HClO_4$ [$\lambda_{max.}$ 570, 430, and 370 nm (sh)].

Metal(II) *Complexes.*—The reaction of nickel(II) carbonate or acetate with $L\cdot 2HClO_4$ gave good yields of $[NiL][ClO_4]_2$. The complex is a 2 : 1 electrolyte in aqueous solution (Λ 209 S cm^2 mol^{-1} at 25 °C). Fractional crystallisation from hot water or water–methanol solutions gave the orange isomer [Aα = N-*rac*-C-*meso* (a–e)] as the least-soluble complex. The n.m.r. spectrum in CD_3NO_2 had signals at 1.24 (d, 3 H) and 1.75 (d, 3 H) p.p.m. assigned to the equatorial and axial methyl groups respectively with an imine methyl signal at 2.20 (6 H) p.p.m.; this later signal is split since the two imine methyls are not exactly equivalent.

The reddish purple copper(II) complex $[CuL][ClO_4]_2$ was prepared by the reaction of copper(II) carbonate with $L\cdot 2HClO_4$. The complex is a 2 : 1 electrolyte in water (Λ 264 S cm^2 mol^{-1} at 25 °C) and the *d–d* spectrum has $\lambda_{max.}$ at 520 nm (ε 86 dm^3 mol^{-1} cm^{-1}) typical of copper(II) complexes of macrocyclic tetra-aza ligands.

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