Cobalt(III) and Rhodium(III) Complexes of *meso*-5,12-Dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene and *meso-meso*-5,12-Dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradecane

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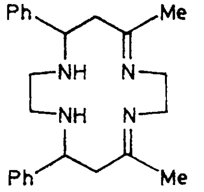
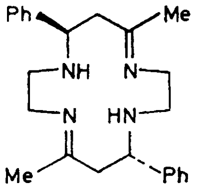
The preparation and properties of the following cobalt(III) and rhodium(III) complexes of the macrocycle *meso*-5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (L^1) and one of the three isomers obtained by $Na[BH_4]$ reduction, *meso-meso*-5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradecane (L^2), are described: *trans*-$[RhCl_2(L^1)][ClO_4]$, *trans*-$[RhCl_2(L^2)]Cl{\cdot}H_2O$, and *trans*-$[RhL^2(OH_2)_2][ClO_4]_3{\cdot}2H_2O$; *trans*-$[CoCl_2(L^1)][ClO_4]$, *trans*-$[CoCl_2(L^1)]Cl{\cdot}3H_2O$, *trans*-$[CoBr_2(L^1)][ClO_4]$, *trans*-$[CoCl(L^1)(NO_2)][ClO_4]$, *trans*-$[CoCl(L^1)(NO_2)]Cl{\cdot}1.5H_2O$, *trans*-$[CoBr(L^1)(NO_2)][ClO_4]$, *trans*-$[CoL^1(NO_2)_2][ClO_4]$, *trans*-$[CoCl_2(L^2)]$-$Cl{\cdot}H_2O$, *trans*-$[CoCl_2(L^2)][ClO_4]$, and *trans*-$[CoBr_2(L^2)]Br{\cdot}2H_2O$.

THE reaction of 1,2-diaminoethane with benzylideneacetone (PhCH:CHCOMe) to give a tetra-aza macrocycle was first reported by Hideg and Lloyd.[1] These workers provisionally assigned the *cis*-di-imine structure (I) to the macrocycle and subsequently provided mass-spectral evidence to support this structure.[2] Cook *et al.*[3] prepared a variety of nickel(II) and copper(II) complexes of this ligand, L^1, and on the basis of n.m.r. work and comparisons with other macrocyclic ligands of known structure suggested that the ligand was the *trans*-C-*meso*-di-imine, (II), in which the two carbon centres have different chiralities (*R* and *S*). Reduction of the di-imine with $Na[BH_4]$ in methanol gives only three tetra-amines (L^2, L^3, and L^4) establishing that the di-imine macrocycle (L^1) is a pure diastereoisomer. A recent crystal-structure determination [4] on $[CuL^2][NO_3]_2$ showed that the complex has the C-*meso*-C-*meso*-N-*meso*-N-*meso* configuration, (III), providing almost unequivocal evidence † for the *trans*-C-*meso* structure, (II), for the macrocyclic di-imine (L^1). The present paper discusses the preparation and properties of some cobalt(III) and rhodium(III) complexes of L^1 and the tetra-amine L^2 obtained by reduction with $Na[BH_4]$. A previous paper[5] described some cobalt(III) complexes of L^1.



(I)



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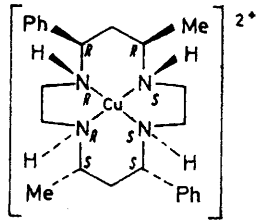

(III)

EXPERIMENTAL

The ligand *meso*-5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (L^1) was prepared as described by Hideg and Lloyd [1] and recrystallised from cyclohexane or light petroleum, m.p. 133—135 °C (Found: C, 76.7; H, 8.5; N, 15.1. Calc. for $C_{24}H_{32}N_4$: C, 76.6; H, 8.5; N, 14.9%).

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† It seems highly improbable that $Na[BH_4]$ reduction in methanol at room temperature would effect a *cis* $\longrightarrow$ *trans* isomerisation.

[1] K. Hideg and D. Lloyd, *Chem. Comm.*, 1970, 929; *J. Chem. Soc.* (*C*), 1971, 3441.

[2] O. H. Hankovsky, K. Hideg, D. Lloyd, and H. McNab, *J.C.S. Chem. Comm.*, 1974, 378.

[3] D. F. Cook, N. F. Curtis, and R. W. Hay, *J.C.S. Dalton*, 1973, 1160.

[4] D. F. Cook and T. N. Waters, *Inorg. Nuclear Chem. Letters*, 1976, **12**, 103.

[5] N. F. Curtis, *J.C.S. Dalton*, 1973, 1212.

meso-5,12-*Dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene Dihydrochloride Monohydrate*, $L^1\cdot 2HCl\cdot H_2O$.—The macrocycle L^1 (1.0 g) was dissolved in cold methanol (7 cm^3 at 0 °C) and the solution treated dropwise with concentrated hydrochloric acid (0.46 cm^3, 2 mol per mol of L^1). When the reaction mixture was cooled in ice the white crystalline *product* slowly formed, and was filtered off, washed with a little acetone, and dried in air, yield 0.6 g (50%) (Found: C, 61.8; H, 8.1; N, 12.1. $C_{24}H_{32}N_4\cdot 2HCl\cdot H_2O$ requires C, 61.7; H, 7.7; N, 12.0%). Attempts to obtain a tetrahydrochloride led to hydrolysis of the imine linkages and the isolation of 1,2-diaminoethane dihydrochloride.

meso-meso-5,12-*Dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradecane*, (L^2).—The compound L^1 (22.5 g, 0.06 mol) was dissolved in warm methanol (*ca.* 250 cm^3) and the solution filtered. Sodium tetrahydroborate (4.5 g, 0.12 mol) was added in small portions over a period of 30 min. The solution was allowed to stand at room temperature for *ca.* 2 h and then filtered. This methanolic solution contains the three isomeric tetra-amines. Isomer L^2 was isolated as follows. The solution was acidified with concentrated HCl (11.6 mol dm^{-3}). The white amine tetrahydrochloride monohydrate which precipitated on standing (*ca.* 30 min) was filtered off, washed with methanol, and dried, yield 28 g. The filtrate and washings contain the hydrochlorides of isomers L^3 and L^4. The free amine L^2 was isolated as follows. The amine tetrahydrochloride monohydrate was dissolved in water–methanol (4 : 1) by warming. Sodium hydroxide solution (2 mol dm^{-3}) was added until the solution just became cloudy, and the solution was then heated on a water-bath. As the methanol evaporated, white crystals of the free amine were deposited. The amine was filtered off, washed with hot water, and twice recrystallised from light petroleum or cyclohexane, m.p. 200—201 °C (Found: C, 75.6; H, 9.5; N, 14.6. $C_{24}H_{36}N_4$ requires C, 75.8; H, 9.5; N, 14.7%). Addition of 2 equivalents of HCl, as described for the diene, gave the dihydrochloride (Found: C, 63.6; H, 8.5; N, 12.3. $C_{24}H_{36}N_4\cdot 2HCl$ requires C, 63.5; H, 8.4; N, 12.4%). Addition of 4 equivalents of HCl gave the amine tetrahydrochloride monohydrate (Found: C, 53.5; H, 7.7; N, 10.2. $C_{24}H_{36}N_4\cdot 4HCl\cdot H_2O$ requires C, 52.9; H, 7.7; N, 10.3%).

trans-*Dichloro*(meso-5,12-*dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*rhodium*(III) *Perchlorate*, *trans*-$[RhCl_2(L^1)][ClO_4]$.—Rhodium trichloride trihydrate (0.26 g, 1.0 mmol) in warm ethanol (30 cm^3) was treated with a solution of L^1 (0.42 g, 1.1 mmol) in warm ethanol (20 cm^3). The solution was immediately boiled and boiling continued for *ca.* 10 min. To the resulting yellow solution, which contained a trace of buff-coloured precipitate, was added water (10 cm^3). The solution was evaporated to *ca.* 30 cm^3 (rotary evaporator), filtered, and treated with aqueous HCl (4 cm^3, 2 mol dm^{-3}), then sodium perchlorate (*ca.* 0.2 g in water). Buff-coloured material, then pale yellow crystals, slowly formed. The yellow *product* was removed by filtration and recrystallised from warm methanol, yield 0.04 g (6%) (Found: C, 44.0; H, 5.0; N, 8.4. $C_{24}H_{32}Cl_3N_4O_4Rh$ requires C, 44.3; H, 4.9; N, 8.6%).

trans-*Dichloro*(meso-meso-5,12-*dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradecane*)*rhodium*(III) *Chloride Monohydrate*, *trans*-$[RhCl_2(L^2)]Cl\cdot H_2O$.—Rhodium trichloride trihydrate (0.26 g, 1.0 mmol) in warm ethanol (30 cm^3) was treated with a solution of L^2 (0.46 g, 1.2 mmol) in warm ethanol (20 cm^3). The mixture was immediately boiled for 10 min, to give a suspension of brown material in a yellow solution. Activated charcoal was then added and the mixture heated and filtered while hot. The clear yellow filtrate was treated with HCl (1 cm^3, 2 mol dm^{-3}), then evaporated to *ca.* 20 cm^3 when a pale yellow crystalline precipitate formed. This precipitate was filtered off and further evaporation of the filtrate gave second and third crops of crystals. The first crop was identified (i.r.) as the tetrahydrochloride of the macrocyclic ligand. The second and third crops were combined and recrystallised from ethanol to which one drop of concentrated HCl had been added, yield 0.20 g (33%) (Found: C, 47.5; H, 6.4; N, 9.1. $C_{24}H_{38}Cl_3N_4ORh$ requires C, 47.4; H, 6.3; N, 9.2%).

trans-*Diaqua*(meso-meso-5,12-*dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradecane*)*rhodium*(III) *Triperchlorate Dihydrate*, *trans*-$[RhL^2(OH_2)_2][ClO_4]_3\cdot 2H_2O$.—The complex *trans*-$[RhCl_2(L^2)]Cl\cdot H_2O$ (0.1 g) and sodium hydroxide (0.1 g) were dissolved in aqueous ethanol (1 : 1, 20 cm^3) and the solution heated under reflux for 30 min. The ethanol was evaporated (rotary evaporator) and the pale yellow solution treated with perchloric acid (3 drops, 70%) giving an almost colourless crystalline precipitate. The crude *product* was recrystallised from aqueous ethanol, adjusted to pH *ca.* 1 with $HClO_4$, to give very pale yellow crystals, yield 0.10 g (71%) (Found: C, 33.6; H, 5.2; N, 6.6. $C_{24}H_{40}Cl_3N_4O_{16}Rh$ requires C, 33.8; H, 5.2; N, 6.6%).

trans-*Dichloro*(meso-5,12-*dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate*, *trans*-$[CoCl_2(L^1)][ClO_4]$.—Cobalt(II) chloride hexahydrate (2.4 g, 10 mmol) was dissolved in methanol (50 cm^3) at room temperature and treated with a solution of L^1 (3.8 g, 10 mmol) in methanol (50 cm^3). The resulting brown solution (exposed to the atmosphere) was allowed to stand for a few minutes and was then treated with hydrogen peroxide (5 cm^3, 10 vol) followed by HCl (20 cm^3, 1 mol dm^{-3}). Perchloric acid (11 cm^3, 1 mol dm^{-3}) was then added dropwise, with stirring, to the green solution. The mixture was allowed to stand for *ca.* 30 min to complete crystallisation. The green *product* was filtered off, washed with a little methanol, then diethyl ether, and dried in air. Yield of crude product, 5.3 g (87%). The complex can be recrystallised in high yield from hot methanol containing a little HCl (Found: C, 47.6; H, 5.4; N, 9.4. $C_{24}H_{32}Cl_3CoN_4O_4$ requires C, 47.6; H, 5.3; N, 9.3%).

trans-*Dichloro*(meso-5,12-*dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Chloride Trihydrate*, *trans*-$[CoCl_2(L^1)]Cl\cdot 3H_2O$.—The crude perchlorate salt (5.0 g) with concentrated HCl (1 cm^3) was suspended in hot methanol (200 cm^3) and added to a suspension of anion-exchange resin (Amberlite, chloride form, *ca.* 50 g dry weight) in water (*ca.* 50 cm^3). The mixture was warmed and stirred until the complex had dissolved. The anion-exchange resin was removed by filtration and washed with warm methanol until the washings were colourless. The filtrate and washings were evaporated (rotary evaporator) to *ca.* 200 cm^3 when a small quantity of green crystalline material precipitated (unchanged perchlorate salt). This was removed by filtration and discarded. The filtrate was evaporated to *ca.* 20 cm^3, treated with propan-2-ol (10 cm^3), and left to stand overnight. The green crystalline product was filtered off, yield 3.0 g (55%) (Found: C, 48.6; H, 6.4; N, 9.2. $C_{24}H_{38}Cl_3CoN_4O_3$ requires C, 48.3; H, 6.4; N, 9.4%).

trans-*Dibromo*(meso-5,12-*dimethyl*-7,14-*diphenyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate*, *trans*-$[CoBr_2(L^1)][ClO_4]$.—Cobalt(II) bromide hexahydrate (3.3 g, 10 mmol) in methanol (50 cm^3) was treated with L^1 (3.8 g, 10 mmol) in methanol (50 cm^3). Hydrobromic acid (10 cm^3, 1 mol dm^{-3}; 10 mmol) was added and the resulting brown solution (exposed to the atmosphere) was allowed to stand for a few minutes. Hydrogen peroxide (5 cm^3, 10 vol) was then added. Addition of $HClO_4$ (11 cm^3, 1 mol dm^{-3}) gave the lime-green *product* which was isolated as described for the corresponding dichloro-derivative. Yield of crude complex, 6.1 g (87%). Recrystallisation from methanol containing a little hydrobromic acid gave the pure *product* (Found: C, 41.7; H, 4.8; N, 8.3. $C_{24}H_{32}Br_2ClCoN_4O_4$ requires C, 41.5; H, 4.6; N, 8.1%).

trans-*Chloro*(meso-*5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene*)*nitrocobalt*(III) *Perchlorate*, *trans*-$[CoCl(L^1)(NO_2)][ClO_4]$.—To *trans*-$[CoCl_2(L^1)][ClO_4]$ (0.61 g) in boiling methanol (250 cm^3), sodium nitrite (0.07 g, 1 mol per mol of cobalt complex) in a little water was added dropwise with stirring. The resulting red-brown solution was filtered, evaporated to *ca.* 30 cm^3 (rotary evaporator), and the brown crystalline *product* filtered off and washed with a little methanol. The crude material was recrystallised from hot methanol (250 cm^3) containing concentrated HCl (3 drops) to give pink crystals, yield *ca.* 0.3 g (*ca.* 50%) (Found: C, 46.9; H, 5.3; N, 11.2. $C_{24}H_{32}Cl_2CoN_5O_6$ requires C, 46.8; H, 5.2; N, 11.4%).

trans-*Chloro*(meso-*5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene*)*nitrocobalt*(III) *Chloride Sesquihydrate*, *trans*-$[CoCl(L^1)(NO_2)]Cl\cdot1.5H_2O$.—To *trans*-$[CoCl_2(L^1)]Cl\cdot3H_2O$ (1.2 g) in methanol (10 cm^3), sodium nitrite (0.14 g, 1 mol per mol of cobalt complex) in water–methanol (3 : 10) was added dropwise with stirring. The solution became brown, then reddish brown on warming. Concentrated HCl (0.5 cm^3) was added, the solution was briefly boiled, and then evaporated to *ca.* 10 cm^3 (rotary evaporator). The resulting solution was allowed to crystallise overnight (scratching with a glass rod may be necessary). The crude *product* was filtered off and recrystallised from water–methanol (1 : 4) containing a few drops of HCl. Scratching and the addition of propan-2-ol may be necessary to initiate crystallisation, yield 0.3 g (*ca.* 25%; there is considerable loss during recrystallisation) (Found: C, 49.8; H, 6.0; N, 12.1. $C_{24}H_{32}Cl_2CoN_5O_2\cdot1.5H_2O$ requires C, 49.7; H, 6.0; N, 12.1%).

trans-*Bromo*(meso-*5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene*)*nitrocobalt*(III) *Perchlorate*, *trans*-$[CoBr(L^1)(NO_2)][ClO_4]$.—This complex was prepared as described for the chloro-analogue, using the dibromo-complex as starting material and HBr in place of HCl. It was necessary to recrystallise the product twice from aqueous methanol to obtain an analytically pure sample (Found: C, 43.7; H, 4.8; N, 10.3. $C_{24}H_{32}BrClCoN_5O_6$ requires C, 43.6; H, 4.8; N, 10.6%).

trans-(meso-*5,12-Dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene*)*dinitrocobalt*(III) *Perchlorate*, *trans*-$[CoL^1(NO_2)_2][ClO_4]$.—The complex *trans*-$[CoCl_2(L^1)][ClO_4]$ (0.60 g) was dissolved in boiling methanol (250 cm^3). Sodium nitrite (0.14 g, 2 mol per mol of Co) in water (2 cm^3) was added dropwise with stirring. The solution was heated for 15 min, filtered, then evaporated to *ca.* 20 cm^3. The yellow product (*ca.* 0.5 g) was filtered off and recrystallised from hot methanol, yield 0.35 g (56%) (Found: C, 46.0; H, 5.2; N, 13.2. $C_{24}H_{32}ClCoN_6O_8$ requires C, 45.9; H, 5.1; N, 13.4%).

trans-*Dichloro*(meso-meso-*5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradecane*)*cobalt*(III) *Chloride Monohydrate*, *trans*-$[CoCl_2(L^2)]Cl\cdot H_2O$.—The hydrochloride $L^2\cdot 4HCl$ (5.3 g, 0.01 mol) was dissolved in the minimum volume of water. Solid $Na_3[Co(CO_3)_3]\cdot3H_2O$ (4.0 g) was added and the mixture heated (water-bath) until effervescence ceased. The solution was filtered and the red filtrate evaporated to small volume. The solution was acidified with concentrated HCl and heated for *ca.* 10 min to ensure complete conversion into the dichloro-complex. The dark green *product* crystallised on cooling and was filtered off, washed with cold water, and dried in air, yield *ca.* 2.8 g (Found: C, 51.2; H, 6.9; N, 9.8. $C_{24}H_{38}Cl_3CoN_4O$ requires C, 51.1; H, 6.8; N, 9.9%).

trans-*Dichloro*(meso-meso-*5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradecane*)*cobalt*(III) *Perchlorate*, *trans*-$[CoCl_2(L^2)][ClO_4]$.—Cobalt(II) chloride hexahydrate (0.24 g) was dissolved in methanol and treated with L^2 (0.38 g) in methanol. The mixture was oxidised in an air stream to give an orange-brown solution. Addition of lithium perchlorate in methanol gave a brown precipitate which on heating with HCl in methanol gave a green solution. The green solution was filtered and on standing the filtrate gave pale green crystals of the product. The complex was washed with cold water and dried in air (Found: C, 47.4; H, 6.1; N, 9.1. $C_{24}H_{36}Cl_3CoN_4O_4$ requires C, 47.3; H, 5.95; N, 9.2%).

trans-*Dibromo*(meso-meso-*5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradecane*)*cobalt*(III) *Bromide Dihydrate*, *trans*-$[CoBr_2(L^2)]Br\cdot2H_2O$.—The complex *trans*-$[CoCl_2(L^2)]Cl\cdot H_2O$ was heated with very dilute ammonia solution, when it dissolved as the pink dihydroxo-complex. The solution was filtered and the filtrate acidified with HBr (48%) and heated for *ca.* 5 min. The lime-green product crystallised on cooling. The complex may be recrystallised by taking up in ammonia and heating with HBr (Found: C, 40.5; H, 4.60; N, 7.7. $C_{24}H_{40}Br_3CoN_4O_2$ requires C, 40.3; H, 5.6; N, 7.8%).

Infrared spectra were recorded on discs (KBr) using a Perkin-Elmer 457 instrument. Electronic spectra were obtained on a Perkin-Elmer 402 instrument, usually with spectroscopic grade methanol as solvent. N.m.r. spectra were recorded at 90 MHz using CD_3CN as solvent with a Perkin-Elmer R32 instrument.

RESULTS AND DISCUSSION

Only a rather limited number of rhodium(III) complexes of macrocyclic tetra-aza ligands have been reported. Complexes of C-*meso*- and C-*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane, L^5 (tet *a*) and L^6 (tet *b*), have been described[6] as have those of 1,4,7,10-tetra-azacyclododecane, L^7 (cyclen),[7] and 1,4,8,11-tetra-azacyclotetradecane, L^8 (cyclam).[8] The ligand L^7 gives only *cis* complexes with Co^{III} and Rh^{III};[7] L^8 gives complexes with Co^{III},[9] Rh^{III},[8] and Cr^{III} [10] in which the amine may be planar or folded, generally with unidentate ligands in the remaining sites. The ligand L^5 gives

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[6] N. F. Curtis and D. F. Cook, *J.C.S. Dalton*, 1972, **691**.

[7] J. P. Collman and P. W. Schneider, *Inorg. Chem.*, 1966, **5**, 1380.

[8] E. J. Bounsall and S. R. Koprich, *Canad. J. Chem.*, 1970, **48**, 1481.

[9] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102; 1966, **5**, 1515; C. K. Poon and M. L. Tobe, *J. Chem. Soc.* (*A*), 1967, 2069; 1968, 1549.

[10] J. Ferguson and M. L. Tobe, *Inorg. Chim. Acta*, 1970, **4**, 109.

trans complexes with Rh^{III} and L^6 gives both *cis* and *trans* complexes.[6]

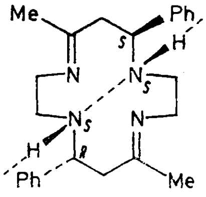
Reaction of $RhCl_3 \cdot 3H_2O$ with L^1 in warm methanol gives low yields of yellow *trans*-$[RhCl_2(L^1)]^+$, isolated as the perchlorate salt. Much higher yields were obtained in the analogous reaction with L^2. The complexes *trans*-$[RhA_2(L^8)]^+$ (A = aniono) undergo facile base hydrolysis,[8] leading to the aquahydroxo- and various anionohydroxo- and anionoaqua-derivatives. Refluxing *trans*-$[RhCl_2(L^2)]Cl$ with Na[OH] in aqueous ethanol gave high yields (>70%) of the very pale yellow *trans*-$[RhL^2(OH_2)_2][ClO_4]_3 \cdot 2H_2O$. Similar observations [6] have been made with L^5 and L^6, but crystalline complexes have not been isolated.

The visible spectra of macrocyclic N_4 complexes normally resemble those of previously reported [6] rhodium(III) tetra-amine complexes, and the characteristic differences between *cis* and *trans* complexes (higher absorption coefficients and lowest-energy band shifted to higher frequency for *cis* complexes compared with the analogous *trans* complex) were used for confirmation of the assigned structures. Thus *trans*-$[RhCl_2(L)]^+$ (L = N_4 macrocycle) complexes usually have $\nu_1(^1T_{1g} \leftarrow {}^1A_{1g}$ of $O_h)$ in the range 24 300—24 600 cm^{-1} with ε 75—120 $dm^3\ mol^{-1}\ cm^{-1}$; *trans*-$[RhCl_2(L^1)]^+$ has ν_1 at 24 900 cm^{-1} (ε 123 $dm^3\ mol^{-1}\ cm^{-1}$) and *trans*-$[RhCl_2(L^2)]^+$ at 24 700 cm^{-1}. The ligand-field strengths of L^1 and L^2 are higher than for L^5 and L^6 (which are comparable to NH_3) and somewhat higher than L^8.

Cobalt(III) *Complexes*.—A number of cobalt(III) complexes of L^1 have been described previously,[5] although the yields are low in a number of cases. This ligand gives *trans*-$[CoL^1X_2]^{n+}$ complexes with X = Cl, Br, NCS, or $MeCO_2^-$ and *cis* complexes with bidentate ligands such as 1,2-diaminoethane (en) and pentane-2,4-dionate (pd). Similar *cis* complexes are formed with the related macrocyclic diene 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene.[5,11]

The relative ease of folding is strong evidence for the *transoid*-diene structure for L^1 shown in (II). For L^1 the N-*rac* (α) configuration (IV) is expected to be highly strained in planar co-ordination. Metastable planar α-configuration complexes of L^1 were prepared for Ni^{II} by unfolding α-configuration complexes (with bidentate ligands) under acidic conditions which preserved the nitrogen configuration.[3] Thus all the *trans*-dianiono-complexes of L^1 with Co^{III} and Rh^{III} are believed to have the N-*meso* (β) configuration, (V). The broken line shown in (IV) indicates the folding axis for the α configuration. Attempts to prepare metastable α-planar complexes of L^1 with Co^{III} have been unsuccessful due to the resistance to acid hydrolysis of the *cis*-$[CoL^1(pd)]^{2+}$ and *cis*-$[CoL^1(en)]^{3+}$ complexes and the inability to prepare the carbonato-complex.[5]

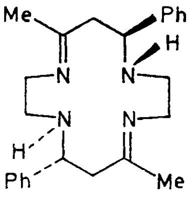
The complex *trans*-$[CoCl_2(L^1)][ClO_4]$ was prepared in high yield (87%) by the reaction of cobalt(III) chloride in methanol with the ligand followed by oxidation with hydrogen peroxide. A similar route was used to synthesise the *trans*-dibromo-derivative, the other complexes being prepared by anion substitution. One aim of the present work was to prepare complexes suitable for kinetic investigations since currently there is considerable interest in the kinetics and mechanism of substitution reactions of dianionocobalt(III) complexes of macrocyclic ligands.[12] The perchlorate salts are practically insoluble in water so that a number of chloride and bromide salts were prepared and these have satisfactory solubilities.



(IV)

C-*meso*-N-*rac*

α configuration



(V)

C-*meso*-N-*meso*

β configuration

The i.r. spectra of the complexes have bands assignable to ν(NH) at *ca.* 3 200 cm^{-1}, ν(C=N) at *ca.* 1 660 cm^{-1}, and to the aromatic substituents of the ligand. The complexes formulated as hydrates show ν(OH) and δ(HOH) absorptions. The electronic spectra are summarised in the Table. In general, only the lowest-energy transition $^1E_g \leftarrow {}^1A_{1g}$ in D_{4h} for the *trans* complexes was observed free of charge-transfer or ligand absorption. The observed energies and intensities support the assignment of *trans* structures to the dianiono-complexes. As observed with the nickel(II) and rhodium(III) complexes, the ligand-field strength of L^1 is greater than for 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (L^9) for which the dibromo-derivative has $\lambda_{max.}$ 672 nm. Since the base strength of L^1 would be expected to be less than the hexamethyldiene due to the replacement of the electron-donating *gem*-dimethyl groups by electron-withdrawing phenyl groups, it appears that interaction between the axial ligands and the *gem*-dimethyl groups leads to a significant decrease in the ligand-field strength of L^9.

Electronic spectra

Complex	$\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})	Solvent
trans-$[RhCl_2(L^1)][ClO_4]$	402 (123)	MeOH
trans-$[RhCl_2(L^2)]Cl \cdot H_2O$	405	MeOH
trans-$[CoCl_2(L^1)]Cl \cdot 3H_2O$	620 (63)	40% MeOH–H_2O
trans-$[CoBr_2(L^1)][ClO_4]$	659	MeOH
trans-$[CoCl(L^1)(NO_2)]Cl \cdot 1.5H_2O$	512 (125)	MeOH, 0.2 mol dm^{-3} in HCl
trans-$[CoBr(L^1)(NO_2)][ClO_4]$	525	MeOH + drop HBr
trans-$[CoL^1(NO_2)_2][ClO_4]$	446	MeOH

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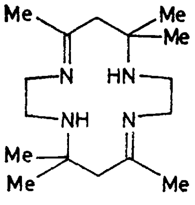
[11] N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *Inorg. Chem.*, 1967, **6**, 770.

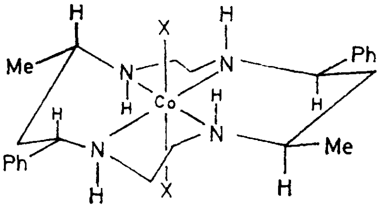
[12] See for example C. K. Poon, *Co-ordination Chem. Rev.*, 1973, **10**, 1.

The crystalline chloride or perchlorate salts of *trans*-$[CoCl(L^1)(NO_2)]^+$, which are initially pink in colour, become brown on standing on the bench possibly due to a photochemical reaction. The complex undergoes rapid aquation in solution (0.01 mol dm^{-3} HNO_3) with $\lambda_{max.}$ changing from 512 to 477 nm, the change being complete in *ca.* 5 min at room temperature. A methanolic solution of the chloride salt with added HCl turns green after 2—3 d, indicating conversion into *trans*-$[CoCl_2(L^1)]^+$.



(L^9)

Complexes of L^2.—The ligand L^2 has the C-*meso*-C-*meso* stereochemistry and it is likely that the most stable form of the *trans*-$[CoX_2(L^2)]^+$ (X = Cl and Br) complexes has the N-*meso*-N-*meso* configuration at the chiral nitrogen centres found with the planar $[CuL^2]$-$[NO_3]_2$ complex. This stereochemistry is shown in (VI) where the Ph and Me groups occupy equatorial positions, the six-membered rings have boat conformations, and the five-membered rings are *gauche*.



(VI)

The ligand L^2 folds with difficulty, base being required to invert the chiral nitrogen centres. The complex *trans*-$[CoCl_2(L^2)]^+$ was readily prepared by reacting the ligand tetrahydrochloride with $Na_3[Co(CO_3)_3]\cdot 3H_2O$ in water followed by treatment with HCl. This reaction proceeds *via* the red *cis*-$[CoL^2(CO_3)]^+$ species and may well yield *trans* complexes with metastable configurations at the chiral nitrogen centres since the configuration of the folded ligand will be retained in acidic solution. There are a number of precedents for this type of behaviour.[11,13] For this reason a sample of green *trans*-$[CoCl_2(L^2)][ClO_4]$ was prepared by aerial oxidation of a methanolic solution of L^2 and cobalt(II) chloride, followed by treatment with HCl and lithium perchlorate. The complex prepared by aerial oxidation is pale green in colour while that prepared by the carbonato-route is dark green. Dark green *trans*-$[CoCl_2(L^2)]Cl\cdot H_2O$ has $\lambda_{max.}$ 405 (ε 79), 482 (ε 37), and 632 nm (ε 38 dm^3 mol^{-1} cm^{-1}) in acetonitrile and an almost identical spectrum is obtained for the pale green *trans*-$[CoCl_2(L^2)][ClO_4]$. The n.m.r. spectra in CD_3CN are also identical, showing a Ph singlet at δ 7.428 p.p.m. and an Me doublet at 1.41 and 1.34 p.p.m. (coupling with the CH) at 90 MHz.

The i.r. spectra (KBr discs) are very similar in the 625—1 600 cm^{-1} region (except for ClO_4 bands at 1 100br and 625 cm^{-1}). However, quite marked differences occur in the NH stretching region. Thus the perchlorate salt has a single strong sharp ν(NH) band at 3 210 cm^{-1}, while *trans*-$[CoCl_2(L^2)]Cl\cdot H_2O$ has bands at 3 210, 3 160, 3 060, and 3 040(sh) cm^{-1}, all the absorptions being relatively weak. Hydrogen bonding of the NH groups with the water of crystallisation could lead to the more complex spectrum, but the possibility of diastereoisomers resulting from different configurations at the chiral nitrogen centres cannot be completely excluded.

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[5/1674 *Received*, 29*th August*, 1975]

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