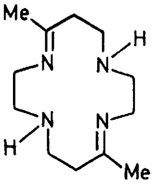
Transition-metal Complexes of the Macrocyclic Ligand *C-meso*-5,12-Dimethyl-1,4,8,11-tetra-azacyclotetradecane

By **Robert W. Hay** * and **Dharam P. Piplani**, Chemistry Department, University of Stirling, Stirling FK9 4LA

Reduction of 5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene dihydroperchlorate with Na[BH$_4$] in methanol–water solution gives predominantly the title ligand (L$_M$). The metal(II) complexes [CuL$_M$][ClO$_4$]$_2$, [NiL$_M$][ClO$_4$]$_2$, [PbL$_M$][NO$_3$]$_2$·1.5H$_2$O, and [ZnL$_M$][ClO$_4$]$_2$ has been prepared. In aqueous solution, spectroscopic measurements show that a planar–octahedral equilibrium $[NiL_M]^{2+} + 2H_2O \rightleftharpoons [NiL_M(OH_2)_2]^{2+}$ occurs with the nickel(II) derivative. The octahedral nickel(II) complexes [NiCl$_2$L$_M$], [Ni(NCS)$_2$L$_M$], and [NiL$_M$(OSMe$_2$)$_2$][ClO$_4$]$_2$ have been characterised. The cobalt(III) complexes *trans*-[CoCl$_2$L$_M$]Cl·2H$_2$O, *trans*-[Co(N$_3$)$_2$L$_M$][N$_3$], *trans*-[CoBr$_2$L$_M$]Br·H$_2$O, and *trans*-[Co(NO$_2$)$_2$L$_M$][ClO$_4$] have also been prepared. *X*-Ray crystallography on the azido-complex confirms that it has the *trans*-(III) or cyclam structure. Ligand folding can occur as indicated by the preparation of *cis*-[RhCl$_2$L$_M$]Cl. *N*-Methylation of L$_M$ with formic acid–formaldehyde gives the *NN'N''N'''*-tetramethyl ligand and complexes of this ligand with Zn^{II} and Cu^{II} have been prepared. The co-ordination chemistry of L$_M$ is discussed and i.r. and *d–d* electronic spectra reported.

A PREVIOUS paper [1] has dealt with some transition-metal complexes of the macrocyclic ligand 5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (L). Reduction of [NiL][ClO$_4$]$_2$ with nickel–aluminium alloy [2] followed by treatment with sodium cyanide gives two isomeric tetra-amines, m.p. 144—145 and 109—110 °C. On the basis of the m.p.s and the similarities of the electronic-absorption spectra of the copper(II) complexes with those of the *C-meso-* and *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecanes described by Curtis,[3] it is possible to provisionally assign the *C-meso* stereochemistry to the isomer having m.p. 144—145 °C and the *C-rac* stereochemistry to the isomer having m.p. 109—110 °C. This assignment has now been confirmed by *X*-ray crystallography on a cobalt(III) complex (see later).



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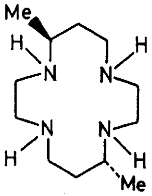
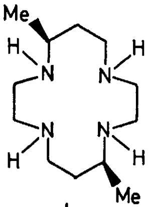


L$_M$



L$_R$

The present paper discusses some aspects of the co-ordination chemistry of *C-meso*-5,12-dimethyl-1,4,8,11-tetra-azacyclotetradecane (L$_M$) and its *NN'N''N'''*-tetramethyl derivative. Two recent papers have dealt with thermodynamic and kinetic studies of L$_M$ with Cu^{II} and Ni^{II}.[4,5] In addition, complexes of a number of other dimethyl-1,4,8,11-tetra-azacyclotetradecanes have recently been studied. The nickel(II) complexes of the 5,7-dimethyl derivative have been investigated by Holtman and Cummings [6] and complexes of the 2,3-dimethyl derivative by Busch and his co-workers.[7]

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

[2] R. A. Kolinski and B. Korybut-Daszkiewicz, *Bull. Acad. polon. Sci.*, 1969, **17**, 13.

[3] N. F. Curtis, *J. Chem. Soc.*, 1964, 2644.

[4] F. P. Hinz and D. W. Margerum, *Inorg. Chem.*, 1964, **13**, 2941.

[5] C-T. Lin, D. B. Rorabacher, G. R. Cayley, and D. W. Margerum, *Inorg. Chem.*, 1975, **14**, 919.

[6] M. S. Holtman and S. C. Cummings, *Inorg. Chem.*, 1976, **15**, 660.

[7] S. C. Jackels, K. Farmery, E. K. Barefield, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, 1972, **11**, 2893.

EXPERIMENTAL

5,12-Dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene dihydroperchlorate $L\cdot 2HClO_4$ was prepared essentially as described by Kolinski and Korybut-Daskiewicz.[2]

C-meso-5,12-*Dimethyl*-1,4,8,11-*tetra-azacyclotetradecane*, L_M.—Freshly prepared $L\cdot 2HClO_4$ (30 g, 0.07 mol) was suspended in methanol–water (300 cm^3, 1 : 1 v/v). A slight excess of sodium tetrahydroborate (6 g, 0.16 mol) was added in small portions over a period of 1 h with continuous stirring. (The solution clears rapidly on the addition of $Na[BH_4]$.) The resulting solution was warmed on a water-bath for *ca.* 20 min until effervescence ceased, and was then allowed to stand for 0.5 h. Crystallisation began during this period. The solution was concentrated on a water-bath and the resulting solid was filtered off, then dissolved in methanol–water. Sodium hydroxide solution (2 mol dm^{-3}) was added to bring the pH to *ca.* 12. Evaporation of the resulting solution on a water-bath gave the crude tetra-amine which was recrystallised from xylene and dried *in vacuo*, m.p. 144—145 °C (lit.,[2] 144.5—145 °C) (Found: C, 62.8; H, 12.2; N, 24.6. Calc. for $C_{12}H_{28}N_4$: C, 63.1; H, 12.35; N, 24.5%).

(*C*-meso-5,12-*Dimethyl*-1,4,8,11-*tetra-azacyclotetradecane*)-*copper*(II) *Perchlorate*, $[CuL_M][ClO_4]_2$.—Copper(II) perchlorate hexahydrate (0.3 g) was dissolved in water (10 cm^3) and added to L_M (0.4 g) in methanol (30 cm^3). A few drops of perchloric acid (70%) were added and the mixture was heated on a water-bath for 30 min. The solution was filtered while hot and the filtrate was concentrated on a rotary evaporator. The crude *product* so obtained was recrystallised from the minimum volume of hot methanol. Cooling in ice gave shiny purple-red plates, which were filtered off, washed with a little ice-cold methanol, then diethyl ether, and dried *in vacuo* (Found: C, 29.6; H, 5.3; N, 11.3. $C_{12}H_{28}Cl_2CuN_4O_8$ requires C, 29.9; H, 5.75; N, 11.4%).

(*C*-meso-5,12-*Dimethyl*-1,4,8,11-*tetra-azacyclotetradecane*)-*nickel*(II) *Perchlorate*, $[NiL_M][ClO_4]_2$.—Nickel(II) perchlorate hexahydrate (0.3 g) and L_M (0.4 g) in methanol–water (300 cm^3, 1 : 1 v/v) containing a few drops of $HClO_4$ (70%) were heated on a water-bath for *ca.* 1 h. The resulting orange-yellow solution was filtered while hot and concentrated to *ca.* 2 cm^3 on a rotary evaporator. Addition of methanol (15 cm^3) followed by subsequent cooling in ice gave orange-yellow crystals which were filtered off. The crude product was recrystallised from hot aqueous methanol and dried in *vacuo* (Found: C, 29.6; H, 5.9; N, 11.25. $C_{12}H_{28}Cl_2N_4NiO_8$ requires C, 29.7; H, 5.8; N, 11.55%).

Isolation of Nickel(II) *Complexes after Reduction with Nickel–Aluminium Alloy*.—The complex $[NiL][ClO_4]_2$ was reduced with nickel–aluminium alloy essentially as described [2] and the solution worked-up by the two methods outlined below.

Method (*a*). The solution obtained after reduction was acidified to pH 2—3 with concentrated hydrochloric acid rather than to pH 8—9 as suggested by Kolinski. At pH 2—3 a violet nickel(II) complex crystallised from the solution. This complex was filtered off and recrystallised from methanol. The i.r. spectrum of the complex has a strong ν(NH) band at 3 235 cm^{-1} while the band at 1 660 cm^{-1} [ν(C=N)] which occurs in the diene complex is absent (Found: C, 40.2; H, 7.7; N, 15.55. $C_{12}H_{28}Cl_2N_4Ni$ requires C, 40.3; H, 7.9; N, 15.65%). The violet dichloro-complex was decomposed as follows. The complex (0.3 g) was dissolved in water and solid sodium cyanide (0.6 g) added. The solution was heated under reflux for 1 h, then evaporated to dryness on a rotary evaporator. The solid residue was extracted with hot benzene, and the benzene evaporated to give the macrocyclic amine which was re-recrystallised from xylene, m.p. 144 °C, confirming that the complex is a derivative of the C-*meso* tetra-amine. The octahedral dichloro-complex is useful for the preparation of a number of other nickel(II) complexes. The dichloro-complex dissolves in water to give an orange solution. Heating the orange solution with added sodium perchlorate gave red (least soluble) and yellow isomers of $[NiL_M][ClO_4]_2$. The yellow isomer appears to have a metastable arrangement of the chiral nitrogen centres since on heating with ammonia solution conversion into the red isomer occurred. Addition of a concentrated aqueous solution of potassium thiocyanate to an aqueous solution of $[NiL_M]Cl_2$ led to the immediate precipitation of lavender $[Ni(NCS)_2L_M]$ (Found: C, 41.4; H, 6.8; N, 20.6. $C_{14}H_{28}N_6NiS_2$ requires C, 41.7; H, 7.0; N, 20.8%). Addition of a methanolic solution of lithium chloride to a solution of $[NiL_M][ClO_4]_2$ in methanol gave crystals of violet $[NiCl_2L_M]$.

Method (*b*). In this case the solution obtained on reduction with nickel–aluminium alloy was acidified to pH 8—9 and the unchanged alloy and $Al[OH]_3$ were filtered off. The filtrate was evaporated to about half its volume, and on cooling a red nickel(II) complex crystallised from the solution. The i.r. spectrum of the complex has strong bands at 1 100br and 625 cm^{-1} indicating ionic perchlorate and a strong ν(NH) band at 3 220 cm^{-1}; the band at 1 660 cm^{-1} [ν(C=N)] in the diene complex is absent. Analysis indicates $[NiL_M][ClO_4]_2$. Decomposition of the complex with K[CN] as described above gave the C-*meso* tetra-amine, m.p. 137—138 °C.

(*C*-meso-5,12-*Dimethyl*-1,4,8,11-*tetra-aza-cyclotetradecane*)-*zinc*(II) *Perchlorate*, $[ZnL_M][ClO_4]_2$.—Zinc(II) perchlorate hexahydrate (0.4 g) was dissolved in water (10 cm^3) and a slight excess of L_M (0.45 g) in methanol (30 cm^3) was added. The mixture was heated on a water-bath for *ca.* 0.5 h, the hot solution was filtered, and the bulk of the solvent was removed on a rotary evaporator. The white crystalline *product* obtained on cooling was recrystallised from the minimum volume of hot methanol, washed with ice-cold methanol, and dried *in vacuo* (Found: C, 29.6; H, 5.95; N, 11.45. $C_{12}H_{28}Cl_2N_4O_8Zn$ requires C, 29.3; H, 5.9; N, 11.4%).

(*C*-meso-5,12-*Dimethyl*-1,4,8,11-*tetra-azacyclotetradecane*)-*lead*(II) *Nitrate Sesquihydrate*, $[PbL_M][NO_3]_2\cdot 1.5H_2O$.—Lead(II) nitrate (0.3 g, 0.001 mol) dissolved in the minimum volume of water was added to a methanolic solution of L_M (0.23 g, 0.001 mol) and the resulting solution was stirred at 50 °C for *ca.* 0.5 h. The mixture was then heated on a water-bath for 0.5 h and filtered while hot. The bulk of the solvent was removed on a rotary evaporator, diethyl ether was added, and on cooling the cream crystalline *product* separated. It was filtered off, washed with a little cold methanol, then diethyl ether, and dried *in vacuo* (Found: C, 24.3; H, 4.9; N, 14.0. $C_{12}H_{28}N_6O_6Pb\cdot 1.5H_2O$ requires C, 24.6; H, 5.3; N, 14.3%).

trans-*Dichloro*(*C*-meso-5,12-*dimethyl*-1,4,8,11-*tetra-aza-cyclotetradecane*)*cobalt*(III) *Chloride Dihydrate*, *trans*-$[CoCl_2L_M]Cl\cdot 2H_2O$.—Trisodium tris(carbonato)cobaltate(III) trihydrate (0.8 g) and an equivalent amount of L_M were mixed in methanol–water (50 cm^3, 1 : 1 v/v) and heated on a water-bath for 30 min with a few drops of concentrated HCl. The resulting red solution was filtered whilst hot.

Concentrated HCl (25 cm^3) was added and the solution volume was reduced to *ca.* 10 cm^3 on a water-bath. The green *product* began separating as the solution was concentrated. Cooling in ice gave the crude complex which was filtered off and recrystallised from hot 6 mol dm^{-3} HCl, and then from methanol. The shiny green needles were washed with a little ice-cold methanol then diethyl ether, and dried *in vacuo* (Found: C, 33.9; H, 6.9; N, 13.1. $C_{12}H_{28}Cl_3CoN_4{\cdot}2H_2O$ requires C, 33.5; H, 7.5; N, 13.0%).

trans-*Dibromo*(C-meso-5,12-*dimethyl*-1,4,8,11-*tetra-azacyclotetradecane*)*cobalt*(III) *Bromide Monohydrate*, $[CoBr_2L_M]Br{\cdot}H_2O$.—A solution of *trans*-$[CoCl_2L_M]Cl{\cdot}2H_2O$ (0.3 g) in a 10% solution of HBr in methanol (40 cm^3) was heated on a water-bath for *ca.* 15 min and the solution was reduced to small volume (*ca.* 5 cm^3) on a rotary evaporator. Cooling in an ice-bath gave the apple-green product which was recrystallised from hot methanol, washed with diethyl ether, and dried *in vacuo* (Found: C, 25.8; H, 5.2; N, 9.75. $C_{12}H_{28}Br_3CoN_4{\cdot}H_2O$ requires C, 25.6; H, 5.4; N, 9.95%).

trans-(C-meso-5,12-*Dimethyl*-1,4,8,11-*tetra-azacyclotetradecane*)*dinitrocobalt*(III) *Perchlorate*, $[Co(NO_2)_2L_M][ClO_4]$.—A solution of *trans*-$[CoCl_2L_M]Cl{\cdot}2H_2O$ (0.25 g) in methanol was heated with a slight excess of sodium nitrite (0.06 g) on a water-bath for 30 min. The resulting brown solution was filtered whilst hot and a few drops of a saturated aqueous solution of $Na[ClO_4]$ were added. The *product* was obtained as orange-brown crystals on cooling in an ice-bath; these were filtered off, washed with ice-cold methanol, then diethyl ether, and dried *in vacuo* (Found: C, 30.5; H, 6.1; N, 17.3. $C_{12}H_{28}ClCoN_6O_8$ requires C, 30.1; H, 5.9; N, 17.55%.

trans-*Diazido*(C-meso-5,12-*dimethyl*-1,4,8,11-*tetra-azacyclotetradecane*)*cobalt*(III) *Azide*, *trans*-$[Co(N_3)_2L_M][N_3]$.—Sodium azide (0.4 g) was added to *trans*-$[CoCl_2L_M]Cl{\cdot}2H_2O$ (0.3 g) dissolved in methanol (20 cm^3) and the mixture was stirred. The dark green solution became blue-violet and was heated on a water-bath for *ca.* 0.5 h. On cooling, blue-violet crystals of the *product* separated; these were filtered off and recrystallised from the minimum volume of hot water. Another crop of the complex could be obtained by the addition of more $Na[N_3]$ to the mother liquor (Found: C, 34.7; H, 6.8; N, 44.0. $C_{12}H_{28}CoN_{13}$ requires C, 34.9; H, 6.8; N, 44.05%).

cis-*Dichloro*(C-meso-5,12-*dimethyl*-1,4,8,11-*tetra-azacyclotetradecane*)*rhodium*(III) *Chloride*, *cis*-$[RhCl_2L_M]Cl$.—Rhodium(III) chloride trihydrate (0.75 g) and L_M (0.96 g) were dissolved in methanol (250 cm^3) and the solution was heated under reflux for 4 h. During this time the colour of the solution changed from red to pale yellow. The solution was filtered whilst hot and concentrated to *ca.* 10 cm^3. Fine yellow crystals of the *product* were obtained on cooling; these were washed with ethanol, then diethyl ether, and dried *in vacuo* for several hours (Found: C, 33.15; H, 6.6; N, 12.6. $C_{12}H_{28}Cl_3N_4Rh$ requires C, 32.9; H, 6.4; N, 12.8%).

NN′N″N‴-*Tetramethyl Derivatives*.—1,4,5,8,11,12-*Hexamethyl*-1,4,8,11-*tetra-azacyclotetradecane tetrahydrochloride monohydrate*, $L_M'{\cdot}4HCl{\cdot}H_2O$. A solution containing L_M (1.15 g, 5 mmol), formic acid (5 cm^3, 90%), and formaldehyde (2 cm^3, 35%) was heated under reflux for 24 h. Concentrated HCl (5 cm^3) was then added to the resulting pale yellow solution, which was then evaporated to dryness. The crude *product* was recrystallised from aqueous ethanol and dried *in vacuo*, m.p. 296—298 °C (slow decomposition) (Found: C, 43.1; H, 9.4; N, 12.45. $C_{16}H_{42}Cl_4N_4O$ requires C, 42.85; H, 9.4; N, 12.5%).

(1,4,5,8,11,12-*Hexamethyl*-1,4,8,11-*tetra-azacyclotetradecane*)*zinc*(II) *perchlorate monohydrate*, $[ZnL_M'][ClO_4]_2{\cdot}H_2O$. An aqueous solution of $Zn[ClO_4]_2{\cdot}6H_2O$ (0.5 g) in the minimum volume of water was mixed with L_M' (0.4 g) in ethanol (15 cm^3). The white crystalline *product* so obtained was filtered off, washed with a little ice-cold methanol, recrystallised from aqueous methanol, and dried *in vacuo* (Found: C, 33.6; H, 6.9; N, 9.6. $C_{16}H_{38}Cl_2N_4O_9Zn$ requires C, 33.9; H, 6.75; N, 9.9%).

(1,4,5,8,11,12-*Hexamethyl*-1,4,8,11-*tetra-azacyclotetradecane*)*copper*(II) *perchlorate monohydrate*, $[CuL_M'][ClO_4]_2{\cdot}H_2O$. Copper(II) perchlorate hexahydrate (0.4 g) dissolved in water (10 cm^3) was added to L_M' (0.5 g) in methanol (30 cm^3). The resulting blue solution was concentrated to small volume in a slow current of air. During this period a light green crust appeared on the sides of the flask, which slowly became violet. The violet material was removed and recrystallised from the minimum volume of water–methanol to give the light blue *product*, which was dried *in vacuo* (Found: C, 33.6; H, 7.0; N, 9.6. $C_{16}H_{38}Cl_2CuN_4O_9$ requires C, 34.0; H, 6.8; N, 9.9%).

Infrared spectra were determined as KBr discs using a Perkin-Elmer 457 spectrophotometer. Visible-spectral measurements were made with a Perkin-Elmer 402 instrument. N.m.r. studies were carried out at 90 MHz with a Perkin-Elmer R-32 instrument using CD_3NO_2 or $(CD_3)_2SO$ as solvent and $SiMe_4$ as internal standard. Magnetic measurements were made with a Newport magnetic balance using $Hg[Co(CNS)_4]$ as calibrant. Conductivity measurements were carried out at 25 °C on methanol or water solutions using a Portland conductivity meter. The concentrations used were 10^{-3} mol dm^{-3}.

RESULTS AND DISCUSSION

Reduction of 5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene dihydroperchlorate $L{\cdot}2HClO_4$ by $Na[BH_4]$ in methanol solution gives predominantly C-*meso*-5,12-dimethyl-1,4,8,11-tetra-azacyclotetradecane (L_M), m.p. 144—145 °C. Complexes of L_M and L_R (the C-*rac* ligand) contain six chiral centres (two carbon and four nitrogen) so that 20 diastereoisomers (16 racemates and four *meso* forms) are theoretically possible. These are conveniently divided into the C-*meso* (L_M) series and the C-*rac* (L_R) series of complexes. In the C-*meso* series there are six racemates and four *meso* forms, while in the C-*rac* series there are 10 racemates. The various stereoisomers of the C-*meso* series are shown in Scheme 1.

It has been established that the thermodynamically most stable form of complexes of macrocyclic 14-membered secondary amine ligands in the absence of C-methyl-group interactions is (I).[8-11] This structure, often referred to as the cyclam or *trans*-(III) form,[8] minimises hydrogen–hydrogen interactions in the chelate

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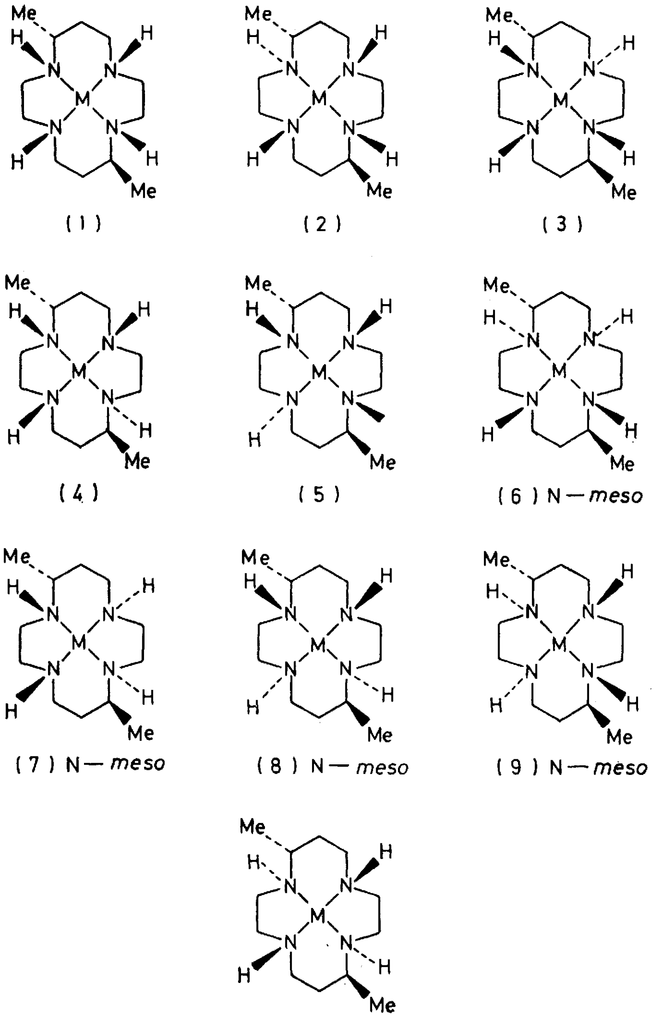
[8] B. Bosnich, M. L. Tobe, and G. A. Webb, *Inorg. Chem.*, 1965, **4**, 1102; B. Bosnich, R. Mason, P. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Comm.*, 1965, 97.

[9] L. G. Warner and D. H. Busch, *J. Amer. Chem. Soc.*, 1969, **91**, 4092.

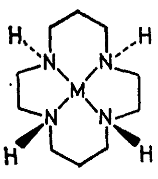
[10] L. G. Warner and D. H. Busch, 'Coordination Chemistry: Papers Presented in Honor of J. C. Bailar, jun.,' Plenum, New York, 1969, p. 1.

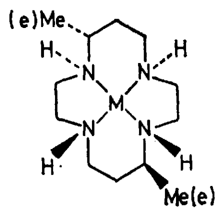
[11] D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, 1970, **92**, 2151.

rings and is virtually free from torsional bond strain. In the C-*meso* ligand this structure also places the two methyl groups in equatorial positions so that the stereochemistry shown in structure (II) is expected to be strongly favoured. *X*-Ray crystallography[12] on *trans*-$[Co(N_3)_2L_M][N_3]$ has confirmed this ligand stereochemistry in the case of the cobalt(III) complex, and has unambiguously established that the amine, m.p. 144—145 °C, is the C-*meso* diastereoisomer.


(1) (2) (3) (4) (5) (6) N—*meso* (7) N—*meso* (8) N—*meso* (9) N—*meso* (10)

SCHEME 1 The C-*meso* series


(I)


(II)

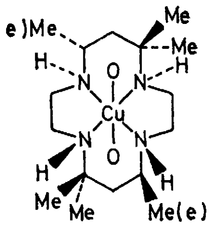
Metal(II) *Complexes*.—A number of metal(II) complexes, $[CuL_M][ClO_4]_2$, $[NiL_M][ClO_4]_2$, $[ZnL_M][ClO_4]_2$, and $[PbL_M][NO_3]_2{\cdot}1.5H_2O$, are readily prepared by treating the appropriate metal salt with the ligand in methanol-water solution. The copper(II) complex is purple-red and has a single *d–d* band at 19 700 cm^{-1} (ε 92 dm^3 mol^{-1} cm^{-1}), Table 1. The wavelength and intensity of this band are comparable to values reported for copper(II) complexes of related tetra-aza-macrocycles.[2,11] Thus C-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane reacts with Cu^{II} in neutral or slightly acidic solution to give a kinetically controlled blue complex with a *d–d* band at 16 100 cm^{-1} (ε 193 dm^3 mol^{-1} cm^{-1}) which at pH 8—9 is readily converted into the thermodynamically stable red isomer with a *d–d* band at 19 600 cm^{-1} (ε 132 dm^3 mol^{-1} cm^{-1}). *X*-Ray work[13] on the perchlorate salt of the red species establishes that it has the *trans*-(III) structure (III). An oxygen atom of each perchlorate group lies in the remaining two octahedral sites, and the copper–oxygen distances (2.59 Å) are indicative of significant bonding interactions. Attempts to prepare an analogous 'blue' copper(II) complex of L_M were unsuccessful. The i.r. spectrum of $[CuL_M][ClO_4]_2$ in the solid state suggests that only ionic perchlorate is present as there is no observable splitting of the ν_{asym} (Cl–O) band at 1 100 cm^{-1}.

TABLE 1

Electronic spectra[a]

Complex	*d–d* Transitions
$[CuL_M][ClO_4]_2$	508(92)
$[NiL_M][ClO_4]_2$ (red isomer)	467(64) in $MeNO_2$
$[Ni(NCS)_2L_M]$	333(14), 510(9.5) in MeOH
trans-$[CoCl_2L_M]Cl{\cdot}2H_2O$[b]	624(33), 450 (sh) (39), 316 (sh) (2 200)
trans-$[Co(N_3)_2L_M][N_3]$	564(420)
trans-$[Co(NO_2)_3L_M][ClO_4]$	442(185)
trans-$[CoBr_2L_M]Br{\cdot}H_2O$[c]	652(53), 385(96)
cis-$[RhCl_2L_M]Cl$	356(258), 305(340)

[a] Band maxima in nm with absorption coefficients (dm^3 mol^{-1} cm^{-1}) in parentheses. Spectra were recorded in aqueous solution unless otherwise specified. [b] In 1 mol dm^{-3} aqueous HCl. [c] In acetonitrile.



(III)

Conductivity measurements on aqueous solutions confirm that the complex is a 2 : 1 electrolyte (Λ 212 S cm^2 mol^{-1} at 25 °C) in this solvent.

The lead(II) complex $[PbL_M][NO_3]_2{\cdot}1.5H_2O$ has i.r. bands (Table 2), due to ν(OH) and δ(HOH), and bands at 1 350, 830, and 710 cm^{-1} due to ionic nitrate. The i.r. spectrum of the zinc(II) complex $[ZnL_M][ClO_4]_2$ has bands at 1 100br and 626 cm^{-1} consistent with ionic perchlorate. Its n.m.r. spectrum in $(CD_3)_2SO$ solution

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[12] G. Ferguson, R. J. Restivo, and R. W. Hay, to be published.

[13] R. M. Clay, P. Murray-Rurst, and J. Murray-Rust, to be published.

has a single methyl doublet centred at δ 1.10 p.p.m. (*J* 5.5 Hz) establishing that the two methyl groups are in identical environments; the chemical shift of the methyl protons is consistent with an equatorial assignment.

TABLE 2

Infrared spectra (cm^{-1}) *

Compound	ν(N–H)	ν(ClO_4^-)	Other bands
L_M	3 285, 3 258, 3 205		
$[CuL_M][ClO_4]_2$	3 220s, 3 180 (sh)	1 100s, br, 628s	
$[NiL_M][ClO_4]_2$ (red)	3 220s	1 100s, br, 627s	
$[PbL_M][NO_3]_2\cdot1.5H_2O$	3 220s		ν(OH) 3 450br; NO_3 ionic 1 350br (ν_3), 830m *(ν_2), 710w (ν_4)
$[ZnL_M][ClO_4]_2$	3 210s	1 100s, br, 626s	
$[NiCl_2L_M]$	3 230s		
$[Ni(NCS)_2L_M]$	3 205s		2 070 [ν(CN)], 786 [ν(CS)], 480 [δ(NCS)]
trans-$[CoCl_2L_M]Cl\cdot2H_2O$	3 200s		
trans-$[Co(N_3)_2L_M][N_3]$	3 185m		$\nu_1(N_3)$ 2 000vs (ionic + co-ord.)
trans-$[Co(NO_2)_3L_M][ClO_4]$	3 195s	1 100s, br, 625s	$\nu_{asym}(NO_2)$ 1 410, δ(ONO) 826
trans-$[CoBr_2L_M]Br\cdot H_2O$	3 210r		ν(OH) 3 450br
cis-$[RhCl_2L_M]Cl$	3 160s, 3 040s		ν(Rh–N) 501s, $\nu(CH_2)$ 871vs and 835 vs, ν(Rh–Cl) 301vs

* Recorded as KBr discs; s = strong, br = broad, sh = shoulder, and vs = very strong.

Nickel(II) *Complexes*.—The reaction of L_M with $Ni[ClO_4]_2$ in methanol–water solution gave an orange-yellow complex $[NiL_M][ClO_4]_2$. N.m.r. studies on a variety of planar nickel(II) complexes of methyl-substituted tetra-aza-macrocycles has established[14] that equatorial methyl substituents occur at δ *ca.* 1.3 p.p.m. and axial methyl substituents at *ca.* 1.7 p.p.m. The n.m.r. spectrum of the orange-yellow complex in CD_3NO_2 displayed both axial (δ 1.75 p.p.m., *J* 7 Hz) and equatorial (δ 1.25 p.p.m., *J* 7 Hz) doublets of unequal intensities indicating a mixture of stereoisomers.

Reduction of $[NiL][ClO_4]_2$ with nickel–aluminium alloy followed by acidification to pH 2—3 with HCl gave the violet complex $[NiCl_2L_M]$. Decomposition of the complex with K[CN], followed by extraction with benzene (see Experimental section), gave the C-*meso*-tetra-amine, m.p. 144 °C, confirming that the complex is a derivative of the C-*meso*-macrocycle. Further work[15] has established that the nickel(II) complexes of the C-*rac*-macrocycle do not readily add axial ligands, so that the above route provides a useful method for separating the two amines.

The complex $[NiCl_2L_M]$ is paramagnetic (μ 2.94 B.M.* at 21 °C) and dissolves in water to give an orange solution and in methanol to give a violet solution. The visible spectra of both water and methanol solutions indicate that an equilibrium $[NiCl_2L_M] \rightleftharpoons [NiL_M]^{2+} + 2Cl^-$ occurs. Methanol and water solutions have a band at 28 600 cm^{-1} due to the ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$ transition of octahedral Ni^{II}, while a very broad band occurs at *ca.* 20 000 cm^{-1} due to a combination of the ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$ transition of octahedral Ni^{II} and the ${}^1B_{1g} \leftarrow {}^1A_{1g}$ transition of square-planar nickel. This view is also supported by conductance measurements: thus Λ = 66 S cm^2 mol^{-1} in methanol and 221 S cm^{-2} mol^{-1} in water (for 1 : 1 electrolytes, 96—115; 1 : 2 electrolytes, 225—270 S cm^2 mol^{-1} for 10^{-3} mol dm^{-3} solutions). The high conductivity in water indicates that complete ionisation of the chloride ligands occurs, the spectral observations being due to the additional equilibrium $[NiL_M]^{2+} + 2H_2O \rightleftharpoons [NiL_M(OH_2)]^{2+}$ discussed below.

Warming aqueous solutions of $[NiCl_2L_M]$ with added $Na[ClO_4]$ gives, on cooling, red crystals of $[NiL_M][ClO_4]_2$ as the least-soluble complex, plus smaller amounts of a yellow isomer which presumably has a different configuration at one or more of the chiral nitrogen centres.† The yellow isomer is isomerised by base to the red isomer. The n.m.r. spectrum of the red isomer in CD_3NO_2 has a methyl doublet at δ 1.27 p.p.m. (*J* 6.5 Hz) consistent with two equatorial methyl groups and indicating the *trans*-(III) configuration (II). The visible spectrum of the red isomer of $[NiL_M][ClO_4]_2$ in aqueous solution has bands at 29 400 (ε 7.5) and 21 740 cm^{-1} (ε 22 dm^3 mol^{-1} cm^{-1}) consistent with the planar $\rightleftharpoons$ octahedral equilibrium $[NiL_M]^{2+} + 2H_2O \rightleftharpoons [NiL_M(OH_2)_2]^{2+}$. The value of Λ for the aqueous solution is 214 S cm^2 mol^{-1} at 25 °C since both species behave as 2 : 1 electrolytes. In nitromethane solution a single *d–d* band is observed at 21 410 cm^{-1} (ε 64 dm^3 mol^{-1} cm^{-1}), the higher-energy 'octahedral' band being absent. In aqueous solution there is *ca.* 65% of the octahedral species and 35% of the planar species.

The red perchlorate salt reacts with lithium chloride in methanol solution to give $[NiCl_2L_M]$, while addition of potassium thiocyanate to an aqueous solution of $[NiCl_2L_M]$ gives lavender $[Ni(NCS)_2L_M]$. The i.r. spectrum of the thiocyanate derivative has bands at 2 070 [ν(CN)], 786 [ν(CS)], and 480 cm^{-1} [ν(CS)] consistent with the isothiocyanato-structure. The complex is essentially a non-electrolyte in methanol solution (Λ 27.5 S cm^2 mol^{-1} at 25 °C). The *d–d* spectrum in methanol

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* Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

† Kolinski[16] isolated four isomers of $[NiL_M][ClO_4]_2$: α(red), β(yellow), γ(orange), and δ(yellow). The α isomer has the *trans*-(III) structure with both methyl substituents equatorial. The β isomer has the same ring conformation as the α, but has two methyl groups axial and the structure has been confirmed by *X*-ray crystallography. The γ isomer has four NH bonds on one side of the NiN_4 plane, and one axial and one equatorial methyl group. The structure of the δ isomer is not established; the complex is paramagnetic in solution. The γ isomer appears to be the intermediate in the conversion of β into α in the presence of base.

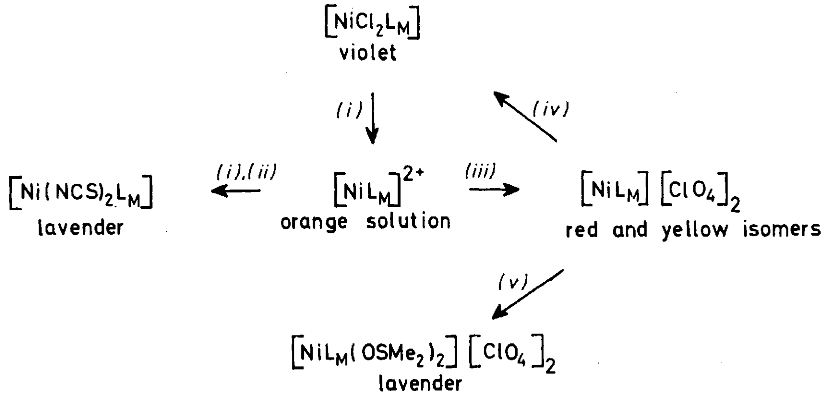
[14] R. A. Kolinski and B. Korybut-Daszkewicz, *Inorg. Chim. Acta*, 1975, **14**, 237.

[15] R. W. Hay and D. P. Piplani, to be published.

[16] R. A. Kolinski, *Abs. 17th Internat. Conf. Co-ordination Chem.*, Hamburg, 6—10th September, 1976; personal communication.

has bands at 30 000 (ε 14) and 19 608 cm^{-1} (ε 9.5 dm^3 mol^{-1} cm^{-1}) which can be assigned to the $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ and $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ transitions in pseudo-octahedral symmetry. Almost identical spectral parameters have been reported[6] for (5,7-dimethyl-1,4,8,11-tetra-azacyclotetradecane)di-isothiocyanatonickel(II) which has bands at 30 769 (ε 16) and 19 608 cm^{-1} (ε 10 dm^3 mol^{-1} cm^{-1}). Attempts to prepare solutions of the red isomer in dimethyl sulphoxide led to the immediate precipitation of lavender $[NiL_M(OSMe_2)_2][ClO_4]_2$, which slowly loses Me_2SO on standing in air. The i.r. spectrum of the complex has the characteristic bands of ionic perchlorate.

The various reactions of the nickel(II) complexes are summarised in Scheme 2.



SCHEME 2 Reactions of the nickel(II) complexes. (i) Water; (ii) K[SCN]; (iii) Na[ClO$_4$]; (iv) LiCl in MeOH; (v) Me_2SO

Cobalt(III) *and Rhodium*(III) *Complexes*.—The complex *trans*-$[CoCl_2L_M]Cl \cdot 2H_2O$ was readily prepared by the reaction of $Na_3[Co(CO_3)_3]$ with L_M in methanol–water solution, in the presence of HCl. A number of other cobalt(III) complexes of the general formulation *trans*-$[CoX_2L_M]^{n+}$ (X = Br, N_3, or NO_2) were prepared by anion-metathesis reactions. Complexes with the *trans*-$[CoX_2N_4]^{n+}$ chromophore (X = Cl) normally exhibit three low-intensity bands in the visible region. Such complexes have a basic D_{4h} symmetry, with the $^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ transition split into two components, $^1A_{1g} \rightarrow {}^1E_g(D_{4h})$ and $^1A_{1g} \rightarrow {}^1A_{2g}(D_{4h})$.[17,18] Where the tetragonal splitting is not very large, *i.e.* if X and N do not differ greatly in position in the spectrochemical series (X = NO_2 or N_3), only a single absorption band is observed under the $^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ envelope. The observed energies and intensities (Table 1) support the assignment of a *trans* configuration. The spectral parameters are very similar to those observed[1] for the analogous complexes of the diene L so that the ligand-field strengths of the two macrocycles are very similar. *X*-Ray crystallography on *trans*-$[Co(N_3)_2L_M][N_3]$ has confirmed the assignment of a *trans* stereochemistry and has established that the ligand has the *trans*-(III) configuration shown in (II). The n.m.r. spectrum of *trans*-$[Co(N_3)_2L_M][N_3]$ in $(CD_3)_2SO$ with tetramethylsilane as internal standard has a methyl doublet centred at δ 1.35 p.p.m. (*J* 6.6 Hz) at 60 MHz which can be assigned to the two equatorial methyl groups, and no other methyl-group signals. Since the complexes were prepared by anion-metathesis reactions in methanol–water solution, inversion at chiral nitrogen centres is unlikely and all the complexes are expected to have the ligand stereochemistry shown in (II). N.m.r. measurements confirm this view, but there appear to be trace amounts of additional isomers in the other cobalt(III) complexes.

A single rhodium(III) complex was prepared by the reaction of $RhCl_3 \cdot 3H_2O$ with L_M in methanol solution. A *cis* configuration can be assigned to yellow $[RhCl_2L_M]Cl$. The *d–d* spectrum has two bands at 28 100 (ε 258) and 32 790 cm^{-1} (ε 340 dm^3 mol^{-1} cm^{-1}). For *cis*-dichloro-(1,4,8,11-tetra-azacyclotetradecane)rhodium(III) the lowest-energy ligand-field band occurs[19] at 28 250 cm^{-1} (ε 223 dm^3 mol^{-1} cm^{-1}) while for the *trans* complex the lowest-energy band occurs[19] at 24 630 cm^{-1} (ε 78 dm^3 mol^{-1} cm^{-1}). Thus the *cis* complexes lacking a centre of symmetry have much higher absorption coefficients and the first ligand-field band occurs at higher energy. The i.r. spectrum provides additional evidence in support of a *cis* configuration. In the *cis*- and *trans*-dichloro-(1,4,8,11-tetra-azacyclotetradecane)rhodium(III) complexes the ν(NH), ν(Rh–N), and CH_2 rocking modes occur as single bands for the *trans* isomer while two bands are observed for the *cis* isomer.[19] For the *cis*-$[RhCl_2L_M]Cl$ complex two ν(NH) bands occur at 3 165 and 3 140 cm^{-1} and two bands are observed at 871 and 835 cm^{-1} assigned to the CH_2 rocking mode. In the folded complexes the expected stereochemistry is that shown in (IV) in which the two axial amine hydrogens point towards the unidentate ligands. The chiral nitrogen centres will have the N-*rac*-N-*rac* stereochemistry shown in (V) with one axial and one equatorial methyl group. Lai and Poon[20] recently confirmed this stereochemistry in *cis*-(ethylenediamine)(1,4,8,11-tetra-azacyclotetradecane)cobalt(III) chloride trihydrate.

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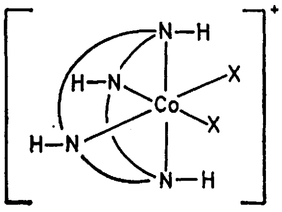
[17] C. K. Jørgensen, 'Absorption Spectra and Chemical Bonding in Complexes,' Pergamon, London, 1962.

[18] R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, 1965, **4**, 709.

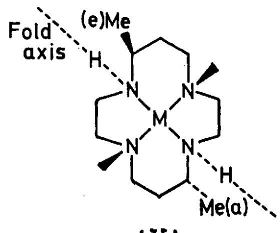
[19] E. J. Bounsall and S. R. Koprich, *Canad. J. Chem.*, 1970, **48**, 1481.

[20] T. F. Lai and C. K. Poon, *Inorg. Chem.*, 1976, **15**, 1562.

NN'N''N'''-*Tetramethyl Derivatives*.—Recently there has been considerable interest in the co-ordination chemistry of *NN'N''N'''*-tetramethyl-1,4,8,11-tetra-azacyclotetradecane and its derivatives since such ligands form complexes which are quite labile, and five-co-ordinate complexes have been observed both in solution and in the solid state.[21] In addition it is possible to obtain kinetically controlled complexes since inversion of secondary nitrogen centres cannot occur in the permethylated ligands.[22,23]



(IV)



(V)

C-*meso*-5,12-Dimethyl-1,4,8,11-tetra-azacyclotetradecane (L_M) is readily methylated by a mixture of formic acid and formaldehyde and the ligand was isolated as the tetrahydrochloride monohydrate $L_M'\cdot 4HCl\cdot H_2O$. The n.m.r. spectrum at 90 MHz [D_2O solution with the sodium salt of 3-(trimethylsilyl)propanesulphonic acid as internal reference] has a doublet centred at δ 1.47 p.p.m. (*J* 7 Hz, 6 H) which can be assigned to the ring methyls split by the ring hydrogen. The *N*-methyl groups occur as two non-equivalent sets due to the presence of the ring methyls with singlets at δ 2.98 (6 H) and 3.07 p.p.m. (6 H).

Kaden and his co-workers[24] recently studied the copper(II) and nickel(II) complexes of L_M' in solution, but did not isolate the solid complexes. Aqueous solutions of $[CuL_M'][ClO_4]_2\cdot H_2O$ are blue-violet in colour with a *d–d* band at 595 nm (ε 192 dm^3 mol^{-1} cm^{-1}). The spectrum is time dependent and slowly changes in a first-order process ($t_{\frac{1}{2}}$ *ca.* 45 min at room temperature) to $\lambda_{max.}$ 630 nm (ε 256 dm^3 mol^{-1} cm^{-1}). The spectral parameters are rather similar to the values reported for (*NN'N''N'''*-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)copper(II) perchlorate where $\lambda_{max.}$ 583 nm (ε 214 dm^3 mol^{-1} cm^{-1}) in nitromethane and 627 nm (ε 227 dm^3 mol^{-1} cm^{-1}) in water. The spectrum reported[24] for the L_M' derivative has $\lambda_{max.}$ 670 nm (ε *ca.* 220 dm^3 mol^{-1} cm^{-1}). Although spectra of copper(II) complexes are not very diagnostic of geometry, it has been suggested that high molar absorption coefficients are indicative of five-co-ordinate structures. The presence of two well defined bands at 1 118 and 1 076 cm^{-1} in the i.r. spectrum of $[CuL_M'][ClO_4]_2\cdot H_2O$ in addition to strong bands at 932 and 623 cm^{-1} is consistent with at least one of the perchlorate anions acting as a unidentate ligand. The value $\Lambda = 80$ S cm^2 mol^{-1} at 25 °C in water is consistent with the formulation as a 1 : 1 electrolyte.

The i.r. spectrum of $[ZnL_M'][ClO_4]_2\cdot H_2O$ has a broad band in the 1 100 cm^{-1} region with no evidence of splitting, suggesting that only ionic perchlorate is present. However, in water at 25 °C, $\Lambda = 92$ S cm^2 mol^{-1} consistent with the formulation as a 1 : 1 electrolyte in this solvent. The n.m.r. spectrum of the complex in $(CD_3)_2SO$ has a doublet centred at δ 1.32 p.p.m. (*J* 7 Hz) and two signals at 2.79 and 2.91 p.p.m. which can be assigned to the two sets of NMe groups in different environments. As the two ring methyls are equivalent (the chemical shift suggests equatorial methyls), a *trans*-(III) structure for the ligand is consistent with the n.m.r. data. Structures in which the four *N*-methyl groups lie on the same side of the co-ordination plane, as has been observed with zinc(II) derivatives of *NN'N''N'''*-tetramethyl-1,4,8,11-tetra-azacyclotetradecane,[21] are excluded by the n.m.r. data. With L_M such structures would give non-equivalent ring methyls, one methyl group axial and the other equatorial.

[6/1790 *Received*, 24*th September*, 1976]

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[21] E. K. Barefield and F. Wagner, *Inorg. Chem.*, 1973, **12**, 2435.

[22] M. J. D'Aniello, M. T. Mocella, F. Wagner, E. K. Barefield, and I. C. Paul, *J. Amer. Chem. Soc.*, 1975, **97**, 192.

[23] F. Wagner and E. K. Barefield, *Inorg. Chem.*, 1976, **15**, 408.

[24] R. Buxtorf, W. Steinmann, and T. A. Kaden, *Chimia*, 1974, **28**, 15.