The $Rh(CO)_2(Q)Cl$ complex was prepared by treating a solution of $(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2$ (0.1 g) in C_6H_6 with benzo(f)quinoline (0.05 g) in C_6H_6. Fine yellow crystals were formed which were filtered and washed with minimum volume of C_6H_6 and dried over fused $CaCl_2$.

Acknowledgement

We are grateful to the U.G.C. (India) for a Research Grant.

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(Received August 10th, 1978) TMC 119

Copper(II), Nickel(II) and Cobalt(III) Complexes of the Macrocyclic Ligand C-*meso*-7,14-Diphenyl-5,6-butano-12,13-butano-1,4,8,11-tetraazacyclotetradeca-4,11-diene

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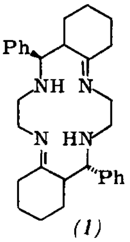
Summary

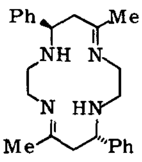
Metal complexes of the macrocyclic tetraaza ligand C-*meso*-7,14-diphenyl-5,6-butano-12,13-butano-1,4,8,11-tetraazacyclotetradeca-4,11-diene** (L) are described. The copper(II) and nickel(II) complexes, isolated as their perchlorate salts, are 4-coordinate species. Several cobalt(III) complexes, *trans*-$[CoLX_2]^+$ ($X = Cl^-, Br^-, NO_2^-$ or N_3^-) have also been characterised. The most probable stereochemistry of the ligand in the metal complexes is the C-*meso*-N-*meso* arrangements of the chiral centres. The N-*meso* stereochemistry leads to the bulky phenyl groups lying in equatorial positions. I.r. and d-d spectra are reported for the various complexes described.

Introduction

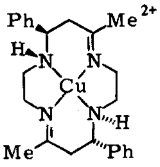
Although a considerable number of macrocyclic ligands are known based on the 1,4,8,11-tetraazacyclotetradecane (cyclam) ring system, the majority of these contain simple alkyl substituents. We have described recently some phenyl$^{(1-2)}$ and thienyl$^{(3)}$ substituted 14-membered macrocycles and their metal complexes. The present paper discusses the preparation of C-*meso*-7,14-diphenyl-5,6-butano-12,13-butano-1,4,8,11-tetraazacyclotetradeca-4,11-diene, L, (*1*), and its complexes with copper(II), nickel(II) and cobalt(III).



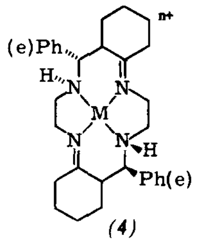
(*1*)



(*2*)



(*3*)



(*4*)

Experimental

Materials

Benzylidene cyclohexanone (*trans*-2-benzalcyclohexanone) was prepared essentially as described by Emerson *et al.*$^{(4)}$. The dibenzylidene derivative is almost insoluble in Et_2O, while the monobenzylidene derivative is quite Et_2O soluble and was hence readily purified, m/e = 186 (Found: C, 84.0; H 7.4. $C_{13}H_{14}O$ calcd: C, 83.8; H, 7.6%).

The ligand (L) was prepared as follows$^{(5)}$. Benzylidene cyclohexanone (18.6 g, 0.1 mol) and 1,2-diaminoethane (6.0 g, 0.1 mol) were heated in a mixture of 2 : 1 v : v cyclo-

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** An alternative nomenclature for the ligand would be C-*meso*-6,17-diphenyl-2,5,13,16-tetraazabicyclo$(16,4,0,0^{7,12})$docosa-1,12-diene.

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hexane : Et_2O for 6 h in the presence of anhydrous K_2CO_3. The solution was filtered and the solvent removed on a rotary evaporator. The residue was suspended in a small volume of Et_2O and allowed to stand in a refrigerator. The solid product was filtered and dried *in vacuo*. The macrocycle has m.p. 140–141°, m/e = 456 with a strong peak at m/e = 396 (M-60), indicating loss of 1,2-diaminoethane. The i.r. spectrum has ν(NH) at 3280 cm^{-1} (Found: C, 78,8; H, 8.7; N, 12.2. $C_{30}H_{40}N_4$ calcd: C, 78.9; H, 8.8; N, 12.3%).

Preparation of metal complexes

The copper(II) complex $[CuL](ClO_4)_2$ was prepared as follows. A slight excess of the ligand (0.3 g) was added to $Cu(ClO_4)_2 \cdot 6H_2O$ (0.15 g) in 1 : 1 v : v MeOH : H_2O (100 cm^3). The mixture was heated on a water bath for *ca.* 20 min, when the solution rapidly turned red purple. The solvent was completely removed on a rotary evaporator and the resulting solid taken up in the minimum vol. of MeOH. Cooling in ice gave reddish purple crystals which were filtered, washed with ice cold MeOH, then Et_2O, and dried *in vacuo.*

The nickel(II) complex was prepared similarly. Analytical and physical data for the complexes are summarised in Table 1. *Trans*-$[CoCl_2L](ClO_4)_2$ 4 H_2O was prepared as follows. The solid ligand (0.3 g) was added to a hot solution of cobalt(II) acetate tetrahydrate (0.2 g) in MeOH (25 cm^3), and the mixture heated on a water bath for *ca.* 30 min. The hot solution was filtered and cooled, and then diluted with 1 : 1 v : v MeOH : H_2O (30 cm^3). The solution was aerated for 20 h, and the MeOH removed on a rotary evaporator. 12 M HCl (4 cm^3) was added to the dull red solution which immediately turned green. The green complex was isolated by slow evaporation on a steam bath followed by cooling in ice. The complex was filtered off, and washed with ice-cold MeOH, then Et_2O, and dried *in vacuo.*

The *trans*-$[CoLBr_2]Br \cdot 4H_2O$ complex was prepared by dissolving the dichloro-complex (0.4 g) in MeOH and treating with 48% HBr (5 cm^3). Removal of the solvent gave the bright green complex (0.3 g).

Trans-$[CoL(N_3)_2](ClO_4) \cdot 2H_2O$ was prepared by dissolving the dichloro-complex in hot MeOH (10 cm^3) and adding two equivalents of NaN_3. The resulting solution was heated on a water bath for 30 min and filtered hot. Addition of $NaClO_4$ solution and cooling gave the required complex, which was washed with a little cold MeOH, then Et_2O, and dried *in vacuo. Trans*-$[CoL(NO_2)_2]ClO_4 \cdot 0.5H_2O$ was prepared similarly using two equivalents of $NaNO_2$.

Physical measurements

The i.r. spectra were determined as discs in KBr on a Perkin-Elmer 457 spectrophotometer. Electronic spectra were measured on a Perkin-Elmer 402 spectrophotometer using H_2O, MeOH, DMSO or MeCN as solvent.

Results and Discussion

The reaction of *trans*-2-benzalcyclohexanone with 1,2-diaminoethane in the presence of potassium carbonate in cyclohexane-ether solvent gives the macrocyclic ligand, L, in good yield. The ligand is expected to have the *trans*-diimine stereochemistry shown in (*1*). The reaction of 1,2-diaminoethane with benzylidene acetone to give the macrocycle (*2*), was originally considered(6) to give the *cis*-diimine, however, more recent work(1, 7–9) including x-ray crystallographic studies of a copper(II) complex(10) has now confirmed the *trans*-diimine stereochemistry shown in (*2*), with the C-*meso* arrangement of the chiral carbon centres. The recent x-ray work(10) has also confirmed the N-*meso* stereochemistry (*3*) of the chiral nitrogen centres in the copper(II) complex. The preferred stereochemistry for metal complexes of L is expected to be as in (*4*) with the C-*meso*-N-*meso* arrangement of the chiral centres. In (*4*) the bulky phenyl groups are equatorial and the cyclohexane rings also lie in equatorial positions.

The conformation of the six-membered rings in diene complexes may be best described as a "sofa" form(11, 12). The accumulated strain caused by the presence of the imine group is believed to be the cause of this distortion from the more energetically favourable chair conformation(12). The five-membered rings formed by the 1,2-diaminoethane residues and the metal atoms are expected to have a *gauche* conformation.

The i.r. spectrum of L has ν(NH) at 3280 cm^{-1} and ν(C=N) at 1640 cm^{-1} with the δ(CH) of the monosubstituted aromatic ring at 700 cm^{-1}. The macrocycle undergoes a quite rapid retro-Michael reaction in absolute ethanol as shown by the interval scan spectrum, Figure 1. The marked increase in absorbance in the region of 246 nm can be attributed to the release of the α,β-unsaturated azomethine or carbonyl chromophore.

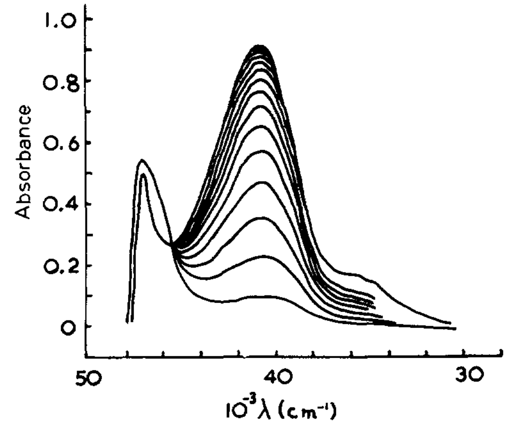

Figure 1. Interval scan spectra of the ligand L (2×10^{-5}mol dm^{-3}) in absolute EtOH in a 2 cm cell at ambient temperature.

Table 1. Analytical and physical data for the complexes

Compound	Colour	Found (Calcd.)%		
		C	H	N
$[CuL](ClO_4)_2$	reddish purple	50.4(50.1)	5.5(5.6)	7.8(7.8)
$[NiL](ClO_4)_2$	yellow	50.0(50.4)	5.7(5.6)	7.6(7.8)
trans-$[CoLCl_2]Cl \cdot 4H_2O$	green	52.0(51.9)	6.5(6.9)	7.9(8.0)
trans-$[CoLBr_2]Br \cdot 4H_2O$	green	43.8(43.6)	5.6(5.8)	6.8(6.8)
trans-$[CoL(N_3)_2]ClO_4 \cdot 2H_2O$	reddish green	48.8(49.0)	5.8(6.0)	19.4(19.1)
trans-$[CoL(NO_2)_2]ClO_4, 0.5H_2O$	orange	50.3(50.3)	5.6(5.8)	11.5(11.7)

Table 2. I.r. (cm^{-1})[a] and electronic (nm) spectral data for the complexes

Compound	ν(NH)	ν(C=N)	$\nu(ClO_4)$	δ (CH)	Other	$\lambda_{max}(\epsilon)$
$\{CuL\}(ClO_4)_2$	3200	1640	1100br, 625	710	–	520(158)[c]
$[NiL](ClO_4)_2$	3240	1640	1100br, 625	710	–	440(146)[d]
trans-$[CoLCl_2]Cl \cdot 4\,H_2O$[e]	[f]	1620	–	712	–	450sh(62)
trans-$[CoLBr_2]Br \cdot 4\,H_2O$[e]	[f]	1620	–	714	–	680(80)[g]
trans-$[CoL(N_3)_2]ClO_4 \cdot 0.5\,H_2O$[e]	3200w	1630	1090br, 622	705	N_3: 2015, 1282	572(618)[g]
trans-$[CoL(NO_2)_2]ClO_4 \cdot 0.5\,H_2O$[e]	3180w	1630	1100br, 627	710	$\nu_{ass}(NO_2)$ 1430 ν(ONO) def. 830	470sh(340)[g]
L	3140	1645	–	700	–	–

[a] KBr discs; [b] monosubstituted aromatic; [c] in DMSO; [d] in MeOH; [e] bands due to ν(OH); [f] obscured by ν(OH)br bands; [g] in dry MeCN; ϵ ($dm^3\ mol^{-1}\ cm^{-1}$).

The metal(II) complexes $[ML][ClO_4]_2$ (M = Cu^{II} and Ni^{II}) were prepared readily. The i.r. spectra of the complexes (Table 2) are consistent with ionic perchlorate. Both complexes show a broad band at 1100 cm^{-1} and a sharp band at 625 cm^{-1} assigned to the assymmetric stretching and bending vibrations of ClO_4^-. The yellow nickel(II) complex has a single d–d band at 440 nm [ϵ = 146 (methanol)] characteristic of square planar nickel(II) complexes with four nitrogen donors, and can be assigned to the ${}^1B_{1g} \leftarrow {}^1A_{1g}$ transition(13). The copper(II) complex has a band at 520 nm [ϵ = 158 (DMSO)]. The wavelength and intensity of this band is comparable to values reported for copper(II) complexes of analogous tetraaza macrocycles(3).

Reaction of the ligand with cobalt(II) acetate in methanol solution followed by aerial oxidation and treatment with hydrochloric acid gives the green *trans*-$[CoCl_2L]^+$ cation, readily isolated as the chloride salt. The *trans*-configuration is indicated by the d–d spectrum with bands at 620 nm (ϵ = 62) and 450 nm (sh, ϵ = 62) in dry acetonitrile. Metathesis in methanol or aqueous solution gave the green *trans*-$[CoLBr_2]Br \cdot 4\,H_2O$, the reddish green *trans*-$[CoL(N_3)_2]ClO_4 \cdot 2\,H_2O$ and the orange *trans*-$[CoL(NO_2)_2]ClO_4$, 0.5 H_2O. The d–d spectra of the complexes are reported in Table 2, and are fully consistent with the *trans*-stereochemistry. The 14-membered tetraaza macrocycles normally only give the folded *cis*-configuration with chelating ligands such as CO_3^{2-} or $acac^-$.

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(Received September 1st, 1978) TMC 126