Electronic Spectra of Some Rhodium(III) Complexes of Saturated Cyclic Tetramines

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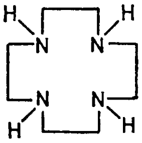
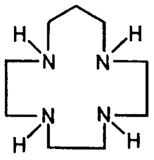
Rhodium(III) complexes of 12-, 13-, 14-, 15-, and 16-membered saturated cyclic tetramines have been synthesised with Cl^- and PF_6^- as counter ions. Molecular formulae for the complexes have been arrived at on the basis of analytical and conductance studies. The stereochemistry of the complexes has been assigned on the basis of electronic spectral data. It is observed that the rhodium(III) complexes are *cis* with 12- and 13-, both *cis* and *trans* with 14-, and only *trans* with 15- and 16-membered ring macrocyclic amines.

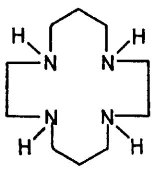
COBALT(III) complexes of saturated cyclic tetramines have been recently studied by Busch and co-workers[1] who observed the formation of configurational isomers and also interconversion of *cis* and *trans* complexes. Rhodium(III) also has a d^6 configuration but is larger than the cobalt(III) ion. Collman and Schneider[2] reported the formation of *cis*-dichlororhodium(III) complexes of L^1 (cyclen) in aqueous solution. Bounsall and Koprich[3] observed that Rh^{III} combines with L^3 (cyclam) in aqueous solution to form only a *cis* complex, but in methanolic solution both *cis* and *trans* isomers were obtained.



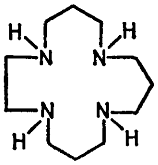
1,4,7,10-tetra-azacyclododecane
L^1 (cyclen)



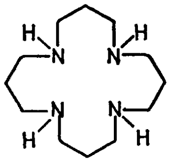
1,4,7,10-tetra-azacyclotridecane
L^2



1,4,8,11-tetra-azacyclotetradecane
L^3 (cyclam)



1,4,8,12-tetra-azacyclopentadecane
L^4



1,5,9,13-tetra-azacyclohexadecane
L^5

Rhodium(III) complexes are inert and hence do not undergo isomerisation easily. Curtis and Cook[4] synthesised rhodium(III) complexes of *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (L^6 or tet a) and the *C-rac* isomer (L^7 or tet b). They observed *cis–trans* interconversion in the case of $[RhL^7I_2]I$, and also indicated the formation of configurational isomers.

In the present work, the synthesis of chlororhodium(III) chlorides with saturated cyclic tetramines (L) has been carried out in methanolic solution using the method adopted earlier for cyclam complexes.[3]

RESULTS AND DISCUSSION

In the case of L^1 and L^2, the complexes $[RhLCl_2]Cl$ (I) separated from methanolic solution. Some of the complex remained dissolved in methanol in the filtrate. This could not be obtained in pure form free from excess of ligand. It was dissolved in water and precipitated as the hexafluorophosphate salt (II) by metathesis with $[NH_4][PF_6]$. With L^3, PF_6 derivatives of both methanol-insoluble (I) and methanol-soluble chloro-complexes (II) were obtained in order to compare their properties with corresponding PF_6 derivatives of L^1, L^2, L^4, and L^5. No insoluble chlororhodium(III) chloride complexes were formed with L^4 and L^5 in methanolic solution. Hexafluorophosphate salts (II) were obtained from the solution as above.

TABLE 1

Complex	Analysis (%) *		
	C	H	N
(1) $[RhL^1Cl_2]Cl$	25.05 (25.2)	5.40 (5.30)	14.5 (14.7)
(2) $[RhL^1Cl_2][PF_6]$	19.4 (19.55)	4.20 (4.10)	11.25 (11.4)
(3) $[RhL^2Cl_2]Cl$	27.05 (27.3)	5.85 (5.60)	13.9 (14.15)
(4) $[RhL^2Cl_2][PF_6]$	21.2 (21.4)	4.50 (4.30)	10.9 (11.1)
(5) $[RhL^3Cl_2][PF_6]$ (*cis*)	23.1 (23.15)	4.80 (4.65)	10.65 (10.8)
(6) (*trans*)	24.0 (23.15)	5.10 (4.65)	10.65 (10.8)
(7) $[RhL^4Cl_2][PF_6]$	24.4 (24.8)	5.10 (4.90)	10.1 (10.5)
(8) $[RhL^5Cl_2][PF_6]$	25.2 (26.35)	5.30 (5.10)	9.40 (10.2)

* Calculated values are given in parentheses.

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The analyses of complexes (I) and (II) correspond to the compositions $RhLCl_5$ and $RhLCl_2(PF_6)$. Molar conductance values of the chloride salts in aqueous solution and of the hexafluorophosphates in CH_3CN solution correspond to 1 : 1 electrolytes (Table 2). This confirms the formulations $[RhLCl_2]Cl$ and $[RhLCl_2][PF_6]$. Rhodium(III) complexes are substitution inert and hence even in aqueous solution the co-ordinated chloride ions are retained.

Absorption Spectra.—Absorption spectra of the chloride salts were obtained in aqueous solution and those of the hexafluorophosphates in CH_3CN solution, scanning the visible and u.v. regions. The band positions and ε values are shown in Table 2.

TABLE 2

Absorption spectra and molar conductances

Complex	ν/cm^{-1} *			$10Dq$/cm^{-1}	Λ/Ω^{-1} cm^2 mol^{-1}
(1)	27 770 (528.4)	33 898 (366.9)		29 307	124.02
(3)	28 571 (443.0)	33 333 (537.8)		29 766	95.62
(2)	27 397 (497)	33 898 (412)		29 022	137.76
(4)	28 571 (306.6)	33 333 (378.7)		29 766	128.8
(5)	28 169 (224.1)	33 333 (365.6)	38 462 (684.1)	29 460	134.03
(6)	25 000 (86.5)				150.17
(7)	23 809 (118.3)	33 333 (292)			150.05
(8)	22 727 (87.8)				

* For solutions in acetonitrile, except for (1) and (3) in water. Values of ε/dm^3 mol^{-1} cm^{-1} are given in parentheses.

Isomers (I) and (II) of $[RhL^3Cl_2]Cl$ have been studied earlier.[3] On the basis of electronic spectra, isomer (I) has been assigned a *cis* structure and (II) a *trans* structure.

In the case of octahedral rhodium(III) complexes there are two spin-allowed transitions ${}^1T_{1g}\leftarrow{}^1A_{1g}$ and ${}^1T_{2g}\leftarrow{}^1A_{1g}$. In *trans* isomers of the type $[RhLCl_2]Cl$ there is tetragonal distortion which leads to four possible transitions as in cobalt(III) complexes:[3,5] ${}^1E_g\leftarrow{}^1A_{1g}$, ${}^1A_{2g}\leftarrow{}^1A_{1g}$, ${}^1B_{2g}\leftarrow{}^1A_{1g}$, and ${}^1E_g\leftarrow{}^1A_{1g}$. The last two are very close in energy. The energy of the second band, ${}^1A_{2g}\leftarrow{}^1A_{1g}$, is equal to $10Dq(xy) - C$ and measures the ligand field along the xy plane.

In *cis* complexes with C_{2v} symmetry, the octahedral model is assumed because of lack of splitting of the ${}^1T_{1g}$ state.[6] Thus for ${}^1T_{1g}\leftarrow{}^1A_g$, $E_1 = 10Dq - C$ and for ${}^1T_{2g}\leftarrow{}^1A_{1g}$ $E_2 = 10Dq + 16B - C$. Bands corresponding to spin-forbidden transitions, ${}^3T_{1g}\leftarrow{}^1A_{1g}$ and ${}^3T_{2g}\leftarrow{}^1A_{1g}$, are of low intensity and could not be seen. It is necessary to have at least three bands to calculate $10Dq$ and C. Since only two spin-allowed bands are observed, C can be calculated using $C = 4B = (1/4)(E_2 - E_1)$,[7] and $10Dq = E_1 + (1/4)(E_2 - E_1)$. Thus for *cis* complexes the bands occur in the higher energy region and the molar absorption coefficients are high due to loss of a centre of symmetry in the complex.

The complex $[RhL^1Cl_2]Cl$ obtained earlier[2] in aqueous solution was assigned a *cis* structure. In the present synthesis, $[RhLCl_2]Cl$ (I) and $[RhLCl_2][PF_6]$ (II), where $L = L^1$ or L^2, also show spectral bands corresponding to a *cis* structure. For L^3, complexes (I) and (II) show bands in the same region as the *cis* and *trans* isomers of $[RhL^3Cl_2]Cl$.[3] The band at 38 461 cm^{-1} appears to be a $N\rightarrow Rh^{III}$ charge-transfer band and has a high ε value. Such charge transfer in other complexes may result in absorption at higher energy. Dq values in the *cis* complexes have been calculated by using the transition energies of the two bands as detailed earlier. The order of Dq (Table 2) is observed to be $L^2 > L^3 > L^1$.

The complexes $[RhL^4Cl_2][PF_6]$ and $[RhL^5Cl_2][PF_6]$ show one band in the visible region as does $[RhL^3Cl_2][PF_6]$ (II). A *trans* structure is suggested for these complexes from the low energy of the band present and its low absorption coefficient. In these complexes the second band corresponding to $10Dq(xy) - C$ is obscured by the charge-transfer bands and hence $Dq(xy)$ could not be calculated. A qualitative comparison of the lowest-energy band shows that in the *trans* complexes the order of the in-plane ligand-field strength is $L^3 > L^4 > L^5$. With the decreasing size of the ring the four nitrogen atoms are closer to the metal ion and create a stronger field.

Thus the present study shows that the geometries of macrocyclic ligand complexes of Rh^{III} are as follows [the geometries of corresponding cobalt(III) complexes are shown for comparison]:

L	Rh^{III}	Co^{III}
L^1	*cis*	*cis*
L^2	*cis*	*cis* and *trans*
L^3	*cis* and *trans*	*cis* and *trans*
L^4	*trans*	*trans*
L^5	*trans*	*trans*

12-, 13-, 15-, and 16-membered rings form similar complexes with both Co^{III} and Rh^{III}. However, L^2 forms both *cis* and *trans* complexes with Co^{III} but only *cis* with Rh^{III}. The reason can be seen in the sizes of Co^{III} and Rh^{III} which are 53 and 67 pm, respectively.[8] The macrocycle L^2 cannot encompass Rh^{III} to form a *trans* complex.

Infrared Spectra.—The i.r. spectra of the complexes were observed as KBr pellets. The *cis* complexes show more bands between 800 and 900 cm^{-1}. There are no significant differences in the bands corresponding to N–H stretching in the *cis* and *trans* complexes.

EXPERIMENTAL

Ultraviolet and visible absorption spectra were obtained using a Cary model 17 spectrophotometer. 1 cm quartz cells were used for the solution spectra. Infrared spectra were recorded on a Perkin-Elmer instrument. Conductivity measurements were performed with an industrial model RC 16 B conductivity bridge at 25 °C on 10^{-3} mol dm^{-3} solutions.

Ligands were synthesised by the methods reported earlier.[9]

Synthesis of 12-, 13-, *or* 14-*Membered Ring Complexes.*—The salt $RhCl_3\cdot 3H_2O$ (0.04 mol) was mixed with an equivalent amount of the macrocyclic ligand (L^1—L^3) in methanol (60 cm^3). The mixture was refluxed for 2 d. The yellow solid obtained was filtered off, washed with methanol, dried, and analysed. The analysis corresponded to the composition $[RhLCl_2]Cl$.

The complex $[RhL^3Cl_2]Cl$ (0.5 g) was dissolved in water (50 cm^3) and precipitated as $[RhL^3Cl_2][PF_6]$ by adding $[NH_4][PF_6]$ (0.25 g). The filtrate after removing $[RhLCl_2]Cl$ was rotoevaporated to dryness and washed several times with chloroform to remove excess of ligand. This solid (0.5 g) was dissolved in water (50 cm^3) and $[NH_4][PF_6]$ (0.25 g) in aqueous solution was added. The solution was warmed and stirred. The yellow precipitate which formed was filtered off, washed several times with water, dried and analysed. The analysis corresponded to the composition $[RhLCl_2][PF_6]$.

Synthesis of 15- *and* 16-*Membered Ring Complexes.*—The salt $RhCl_3\cdot 3H_2O$ (0.04 mol) was mixed with an equivalent amount of macrocyclic ligand (L^4 or L^5). The mixture was refluxed for 3 d. No yellow precipitate appeared. The solution was rotoevaporated to dryness. The resulting solid was washed several times with chloroform to remove excess of ligand then dissolved in water and $[RhLCl_2][PF_6]$ was precipitated as above. The salt $[RhL^4Cl_2][PF_6]$ gave the expected analysis, but $[RhL^5Cl_2][PF_6]$ showed a slightly lower value of carbon and nitrogen than expected. The synthesis was therefore repeated thrice and the best result has been reported. The discrepancy may be due to traces of impurity. Purification might have been possible by column chromatography but the amount of complex available was inadequate.

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