Metal Template Synthesis of Aqua{2,12-Dimethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene}ruthenium(II) Perchlorate

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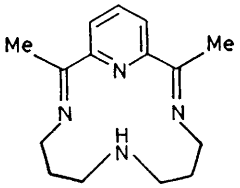
Summary The synthesis and characterization of aqua{2,12-dimethyl-3,7,11,17-tetra-azabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene}ruthenium(II) perchlorate are described; this is the first example in which ruthenium has been used as a template leading to the formation of a macrocyclic Schiff-base amine.

Synthesis of macrocyclic amine complexes *via* metal template reactions has received much attention in recent years.[1–4] All the Schiff-base condensation reactions have largely been effected by metal ions of the first transition series. The use of ruthenium as a template for macrocycle synthesis has never been reported. In fact, relatively few ruthenium macrocyclic amine complexes are known.[5–7] We report here the first example in which ruthenium can also act as a template for the synthesis of L^1.

A ruthenium(II) complex of L^1 was prepared by refluxing an aqueous ethanolic solution (70% ethanol, 50 cm^3) of *mer*-RuL^2Cl_3[8] (L^2 = 3,3'diaminodipropylamine, 2×10^{-3} mol) and 2,6-diacetylpyridine (2×10^{-3} mol), maintained at pH *ca.* 7 (with glacial acetic acid), for *ca.* 6 h. The solution was evaporated to a small volume and a concentrated aqueous solution of $Na[ClO_4]$ was added to crystallize out a dark violet microcrystalline solid (yield 65%). The experimental elemental analytical data are consistent with the empirical formula $[RuL^1(H_2O)][ClO_4]_2$.

The complex is diamagnetic. Its n.m.r. spectrum is very similar to that of *trans*-[CoL^{1}Cl$_2$][ClO$_4$][9,10] (also of t_{2g}^6 configuration), thus confirming a planar disposition of the macrocycle about the ruthenium(II) ion. The i.r. spectrum of the complex is also very similar in the region of the skeletal vibration of the macrocycle to that of *trans*-[CoL^{1}Cl$_2$][ClO$_4$].[9,10] The presence of a sharp $\delta_{\text{Cl-O}}$ band at 620 cm^{-1} (strong) confirms that both perchlorate ions are not co-ordinated to the ruthenium(II) ion even in the solid state. There is some indication that the water molecule, the presence of which was confirmed by the i.r. spectrum, is co-ordinated to the ruthenium(II) ion since it cannot be removed upon drying the complex at 100 °C *in vacuo* for several hours. The far i.r. spectrum clearly denies the presence of any co-ordinated chloride and the total chloride analysis, therefore, must come from the perchlorate ions. The electronic absorption spectrum of the complex in methanol displays strong metal-to-ligand charge-transfer transitions [512(3250) and 562 sh nm (2670)†].



L^1

This complex may be considered either as a five-co-ordinate square pyramidal monomer, [RuL^1(H$_2$O)]-[ClO$_4$]$_2$, or as a dimer containing a Ru–Ru bond, [RuL^1(H$_2$O)]$_2$[ClO$_4$]$_4$. Both structures are not uncommon among ruthenium(II) complexes of porphyrinato-type ligands.[7,11] Unfortunately, we have not been able to obtain the mass spectrum of this charged species, which might distinguish a dimer from a monomer. The conventional molar conductance and molecular weight determinations in solution are not particularly critical since the values obtained depend on whether a monomer or a dimer is assumed in the calculation. For example, the molar conductance of $\Lambda = 253$ ohm^{-1} cm^2 mol^{-1} in aqueous solution at 20 °C is consistent with a 2 : 1 electrolyte based on a monomeric calculation whereas the value of $\Lambda = 506$ ohm^{-1} cm^2 mol^{-1}, on the other hand, is consistent with a 4 : 1 electrolyte based on a dimeric calculation. At present, the structure of the complex has not been determined, although work is now in progress to grow suitable crystals for an *X*-ray crystal structure determination of the complex.

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† Molar absorptions in cm^{-1} dm^3 mol^{-1} are given in parentheses; sh represents shoulder.

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