Binuclear organometallic ruthenium complexes of a Schiff base expanded porphyrin†

Luciano Cuesta, Elisa Tomat, Vincent M. Lynch and Jonathan L. Sessler*

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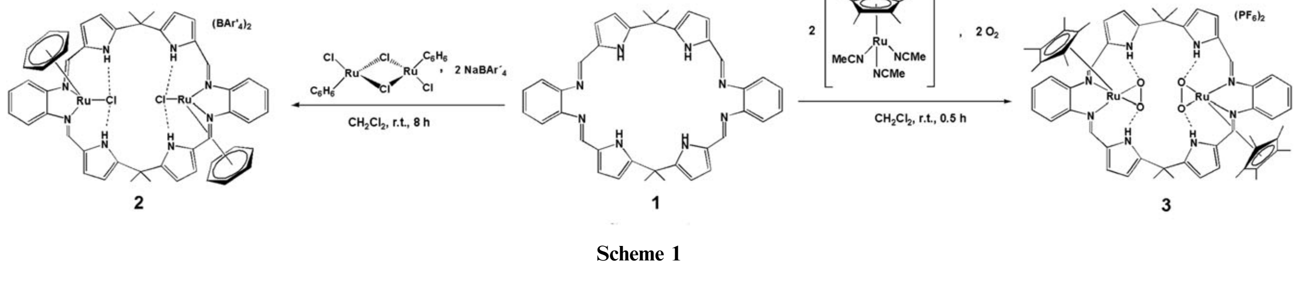
The synthesis of binuclear organometallic ruthenium complexes of an expanded porphyrin-type macrocycle is reported; pyrrolic hydrogen bonding donors were found to interact with ancillary ligands in the primary coordination sphere and to stabilize coordinated dioxygen in an η^2-fashion.

Core-expanded porphyrin analogs constitute a diverse class of macrocyclic ligands that display a range of cavity geometries and sizes, optical properties and coordinative functionalities.[1] Owing to their similarity to natural tetrapyrroles, expanded porphyrins have attracted considerable interest as platforms for the preparation of new metal complexes,[2] as well as the exploration of reactivity patterns that have no known parallel in the case of natural porphyrins. For instance, Schiff-base expanded porphyrin macrocycles have been used to stabilize non-labile 1 : 1 lanthanide complexes,[3] to provide molecular frameworks for the cooperative action of two metals onto one substrate,[4] including positive allosteric binding processes,[5] and, recently, to illustrate an unprecedented reactivity pattern for the uranyl cation.[6] In this communication, we describe the preparation and characterization of a first set of semi-sandwich ruthenium(II) organometallic complexes stabilized by the dipyrromethane-based expanded porphyrin **1** (see Scheme 1). One of these complexes is characterized by unusual hydrogen bonds between the core pyrrole NH's and a metal-bound dioxygen that is apparently without precedent in the chemistry of metalloporphyrins.

A rich array of hydrogen bonding donors (typically pyrrolic NH's) within the macrocyclic cavity represents a defining feature of expanded porphyrins. This aspect of their chemistry is largely responsible for their well-recognized anion binding behavior. However, it is also becoming apparent that related NH hydrogen bonding interactions might contribute to the complexation of metal cations by expanded porphyrin-type ligands.[2] Such non-covalent interactions are essential components of the microenvironments surrounding metal ions within the active sites of natural bioinorganic systems, and are thought to play pivotal roles in mediating the function of numerous enzymes (*e.g.*, heme proteins, superoxide dismutases, lipoxygenases, *etc.*).[7] Recent studies of synthetic metal complexes have elucidated a range of important effects arising from available hydrogen-bonding groups,[8] and the incorporation of both covalent and non-covalent interactions can be regarded as an essential requirement in the design of bio-inspired structures. Such considerations provide an additional incentive to investigate the role of hydrogen bonding interactions in the coordination chemistry of expanded porphyrins. We were particularly eager to assess the effect, if any, such ancillary effects might have on the stabilization of organometallic fragments since this is an area of investigation that remains virtually unexplored.[9]

For our initial investigations, we focused on the stabilization of organometallic "piano-stool" ruthenium(II) complexes using the Schiff-base expanded porphyrin **1**. This choice of organometallic fragments reflects the fact that these species not only have well-defined redox properties, but are also readily amenable to modification, features that have allowed them to be developed as versatile catalysts[10] and as anti-cancer leads.[11] Likewise, the choice of macrocycle **1** reflects the fact that this Schiff-base system, first reported only five years ago,[12] has proven to be a very versatile platform for cation complexation.



Scheme 1

Department of Chemistry and Biochemistry and Institute for Cellular and Molecular Biology, University of Texas, 1 University Station A5300, Austin, TX 78712-0165, USA. E-mail: sessler@mail.utexas.edu

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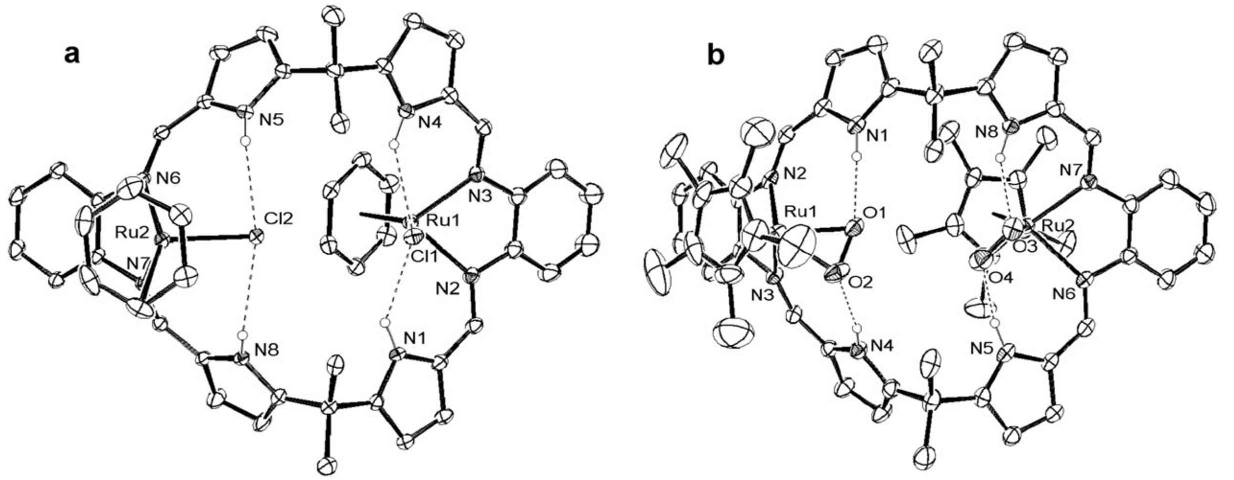

Fig. 1 Top view of the molecular cations present in **2** (panel **a**) and in **3** (panel **b**) showing partial atom-labeling schemes. Displacement ellipsoids are scaled to the 30% probability level. Most hydrogen atoms have been removed for clarity and the dashed lines are indicative of H-bonding interactions. Selected bond distances in complex **2**: Ru(1)–Cl(1): 2.4015(11) Å, Ru(1)–N(2): 2.105(3) Å, Ru(1)–N(3): 2.101(4) Å, Ru(2)–Cl(2): 2.3815(10) Å, Ru(2)–N(6): 2.125(3) Å, Ru(2)–N(7): 2.120(3) Å; selected bond distances in complex **3**: Ru(1)–O(1): 2.023(4) Å, Ru(1)–O(2): 2.056(3) Å, Ru(1)–N(2): 2.148(4) Å, Ru(1)–N(3): 2.096(4) Å, Ru(2)–O(3): 1.989(4) Å, Ru(2)–O(4): 2.036(4) Å, Ru(2)–N(6): 2.103(4) Å, Ru(2)–N(7): 2.186(4) Å.

Treatment of the free base form of macrocycle **1** with an equimolar quantity of the dimeric arene ruthenium complex [$\{Ru(\eta^6\text{-}C_6H_6)(Cl)\}_2(\mu\text{-}Cl)_2$], in the presence of 2 equiv. of NaBAr′$_4$ (Ar′ = 3,5-bis(trifluoromethyl)phenyl) led to the formation of the organometallic binuclear species **2** (see Scheme 1). This air-stable compound was characterized by X-ray diffraction analysis, NMR spectroscopy, elemental analysis, and mass spectrometry. The crystal structure of the binuclear ruthenium complex **2** is shown in Fig. 1a (see also Fig. S1†). The local coordination environment around the Ru atoms can be described in terms of the "piano stool" geometry typical of this kind of Ru(II) semi-sandwich complexes, wherein the arene group is the "seat" and the other ligands, in this case the iminic nitrogen donors of the macrocycle and the chloride ion, provide the "legs".

In complex **2**, the macrocycle adopts a V-shaped structure, in which one of the benzene groups coordinated to the metal center points to the interior face of the cavity, while the other is bound to the "outside" face. As a consequence, the structure of this complex is asymmetrical in the solid state. This loss of symmetry is not evident in the room-temperature ^{1}H and ^{13}C NMR spectra of **2**, where only one set of singlets is found for the pyrrolic NH's, the iminic protons and the methyl groups, as would be expected for a fast equilibrium between two or more conformations in solution.

The NMR spectrum of **2** recorded at 50 °C revealed no appreciable changes. In contrast, at −50 °C the NH and the methyl signals are clearly split into two sets of peaks, consistent with the proposal that the complex is "frozen" into an asymmetric conformation in the solid state.

As observed for other expanded porphyrin ligands,[2] the pyrrolic NH's generate a unique coordination environment inside the macrocyclic cavity and are engaged in strong intramolecular hydrogen bonding interactions with the chloride ligands; this is reflected in the short N···Cl distances (N1···Cl1: 3.143(3) Å, N4···Cl2: 3.107(4) Å, N5···Cl2: 3.062(3) Å, N8···Cl2: 3.067(3) Å) and in the downfield-shifted resonances for the pyrrolic NH's (12.20 ppm in $CDCl_3$).

The tetrapyrrolic macrocycle **1** was also found to react with 2 equiv. of [$Ru(Cp^*)(CH_3CN)_3$][PF_6] (Cp* = pentamethylcyclopentadienyl) at room temperature to afford compound **3**, after exposure to air (see Scheme 1), a species that was characterized by elemental analysis, mass spectrometry, NMR spectroscopy, and X-ray diffraction analysis. The solid state structure of **3** is shown in Fig. 1b (see also Fig. S2†). The complex contains two RuCp* units stabilized within the macrocyclic pocket, which adopts a typical V-shape conformation. Each metal center is coordinated to two iminic nitrogen atoms provided by the macrocycle with the coordination sphere about each ruthenium center being completed through a dioxygen ligand bound in an η^2-fashion. The O–O distances (O(1)–O(3): 1.400(5) Å and O(2)–O(4): 1.316(6) Å) are significantly different, a disparity that is ascribed to a solid state effect. Although both distances are somewhat shorter than what would be expected for a genuine peroxide ligand (the O–O bond length in H_2O_2 is 1.49 Å) we believe that **3** should be formally considered as a binuclear Ru^{IV} complex.

An interesting feature of complex **3** is that the binding of the O_2-derived ligands is assisted by intramolecular hydrogen bonds. This is reflected in the solid state in terms of geometries and distances consistent with such interactions;[13] however, no elongation of the O–O bond distance, relative to other peroxide-dioxygen cationic complexes derived from a {RuCp*} fragment, is observed.[14]

In acetone-*d*$_6$ solution, the signals for the pyrrolic NH's of **3** appear at 13.22 and 13.45 ppm in the ^{1}H NMR spectrum, a finding that is fully consistent with the presence of strong hydrogen-bond interactions.[15] Both the ^{1}H and ^{13}C NMR spectra display two different sets of signals for the Cp* rings and the macrocyclic framework; this provides additional support for the notion that the solid state structure of **3** is retained in solution at room temperature. In contrast to what was observed for the bis-Ru(η^6-C_6H_6) complex **2**, the presence of the bulky Cp* ligands appears to lock the conformation of **3** in solution. Consistent with this latter inference, no significant changes in the proton resonances were observed for the ^{1}H NMR spectrum of **3** recorded at -50 °C (*cf.* Supporting Information†).

The formation of complex **3** takes place even when very small amounts of dioxygen are present. Indeed, all attempts to trap a deoxygenated complex analogous to **3** failed. Apparently, in the absence of a coordinative ligand such as chloride ion (*cf.* complex **2**) or dioxygen (as in the case of complex **3**), the putative Ru(II) complex obtained from the reaction of **1** with [Ru(Cp*)(CH_3CN)$_3$][PF_6] is unstable.

In summary, the Schiff-base tetrapyrrolic macrocycle **1** has been used to prepare two hitherto unprecedented binuclear ruthenium organometallic complexes. In both cases, pyrrolic NH donors on the macrocyclic scaffold are engaged in strong hydrogen-bonding interactions with a ligand bound to the metal center, a chloride anion in the case of **2** and an η^2-bound dioxygen ligand in the case of **3**. These two complexes thus serve to showcase the key role that non-covalent interactions can play in stabilizing new coordination geometries. Studies on the reactivity of complexes **2** and **3** in stoichiometric and catalytic processes, focusing on the potential role that H-bond interactions can play in assisting chemical transformations, are currently underway in our laboratories.

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