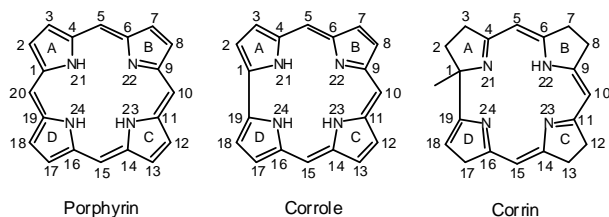


Peculiar behavior of biscoxocorrole and porphyrin-corrole bismacrocycles towards the complexation of transition metals

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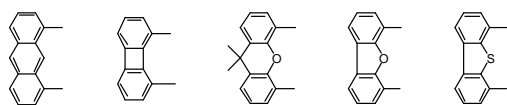
Corroles can be considered as intermediates between porphyrins and corrins since they possess a direct link between two pyrrole units and retain a 18 π electron aromatic system (Scheme 1).



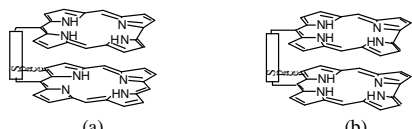
Scheme 1

The chemistry of corroles has been considerably developed during the past fifteen years. This interest stems from their ability to coordinate metal ions in higher oxidation states than porphyrins due to the reduced size of the macrocyclic cavity compared to porphyrins and the presence of three NH groups (Scheme 1). Until today more than 20 metal ions have been inserted into the corrole cavity.

From our side we have been interested in the synthesis of bismacrocycles where one of the two macrocycles is at least a corrole unit. In order to maintain both macrocycles in a face-to-face arrangement, various rigid spacers were investigated (Scheme 2).



Spacers used in the synthesis of porphyrin-corrole and bisoxocorrole derivatives



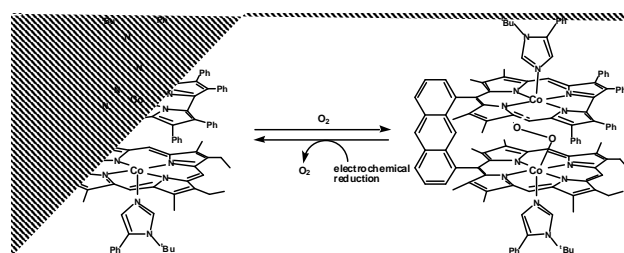
Schematic representation of the porphyrin-corrole (a) and bisoxocorrole skeletons (b) (meso and beta substituents have been omitted for clarity)

Scheme 2

It was previously reported for Pacman porphyrins that mixed valent species of the type Co(II)/Co(III) are good catalysts for the reduction of dioxygen to water *via* a four electron process. However, this mixed valent species must be generated from the starting Co(II)/Co(II) derivative by a chemical or an electrochemical oxidation.

Because of the property of corroles to stabilize high oxidation states of metals, bismacrocycles in a face-to-face arrangement containing one porphyrin and one corrole unit are remarkable precursors for mixed valent compounds. Indeed, it is now relatively easy to directly prepare mixed valent Co(II)/Co(III) derivatives where the Co(II) ion is coordinated to the porphyrin ring and the Co(III) to the corrole moiety.

We have been able to demonstrate using various physicochemical techniques that the Co(II)/Co(III) species is able to reversibly coordinate O₂ in an endo position (Scheme 3).



Scheme 3

The μ -superoxo species described in Scheme 3 is the active species for the catalysis of the four electron reduction of O₂ to water.

Bisoxocorrole derivatives are also of a great interest in order to modelize interactions occurring between two metallic centers in high oxidation states. For example, when these dyads are metalated by nickel in an open air atmosphere, the insertion of an oxygen atom occurs at a *meso* position of each corrole unit and *cis* and *trans* nickel bis(oxocorroles) are formed. The structure of the *cis* isomer has been solved by X-ray diffraction and is given on Figure 1.

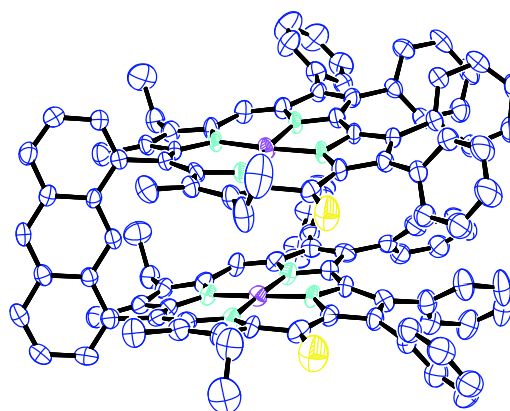


Figure 1

The probable mechanism involving a dioxygen attack at a *meso* position of the corrole units will be detailed.

Conversely, bisoxocorrole derivatives do not form bisoxocorroles when metalated with copper. Biscopper species are readily obtained as shown by the X-ray structure of the biscopper anthracenyl bridged complex reproduced on Figure 2.

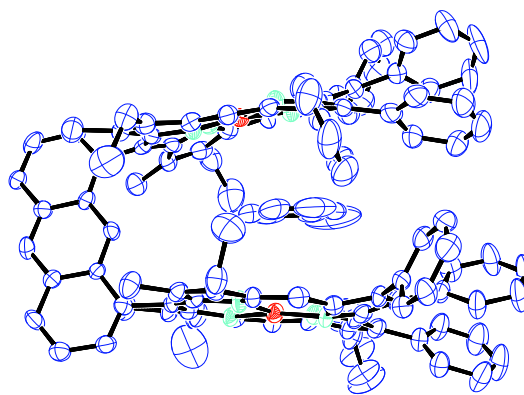


Figure 2

The complete analysis of the physicochemical data will be reported.

Reference

R. Guilard, J. M. Barbe, C. Stern and K. M. Kadish, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Elsevier Science (USA), 2003, vol. 18, in the press.