

Redox behavior of open chain polypyrrolic complexes.

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Redox behavior of aromatic cyclic tetrapyrrolic complexes has been extensively studied during the last decades in the aim to study how structural changes affect their redox behavior. Beside these cyclic tetrapyrrolic systems, biliverdin, a degradation product of heme by oxygenation, is known since 1930 and represents the first example of a conjugated open-chain tetrapyrrolic ligand. This ligand behaves either as a trianion to complex trivalent cations or as a dianion radical to complex divalent cations. An other known open-chain conjugated tetrapyrrolic ligand is formylbiliverdin which behave as a dianion yielding neutral complexes with divalent transition metals. Despite extensive studies, electrochemical investigations on open-chain tetrapyrrolic complexes remain scarce^[1,2].

More recently open chain tetrapyrrolic complexes of divalent transition metals have been synthesized with the bidipyrin ligand shown on figure 1^[3,4] as well as complexes with an open chain tripyrrolic ligand^[5] depicted in figure 2. The goal of our electrochemical investigation on this new class of complexes was to identify the electron transfer sites (ligand versus metal), to study the stability and reactivity of the electrogenerated species and to compare their redox behavior to known systems, namely porphyrins and open chain tetrapyrrolic compounds.

The redox behavior of a series of bidipyrin complexes with palladium, nickel and copper, clearly indicate that these complexes undergo two one-electron reductions as well as two one-electron oxidations, all electron transfers being reversible and ligand centered as shown by spectroelectrochemical investigation. In addition, studies of a series of bidipyrin bearing different substituents in the para position of the phenyl (Fig.3) clearly demonstrate a linear correlation between the observed redox potentials and the Hammett σ values of the substituents as depicted on figure 3. These complexes behave like porphyrins and its isomers. However due to a more flexible structure, the Homo-Lumo gap is much more depending on the nature of the complexed metal and is lying between 1.5 to 1.6V. To get better insights in these new derivatives, further investigations are under way.

The tripyrrolic ligand behave as a monoanion, and is able to complex divalent transition metals. Preliminary results on the redox behavior of tripyrrolic complexes will be presented, and will be compared with literature data.

References.

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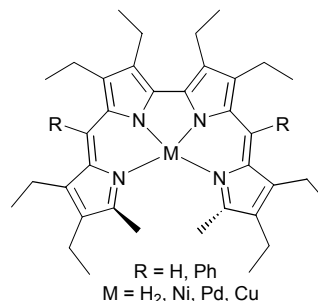


Fig. 1 Structure of octaethyl bidipyrin complexes.

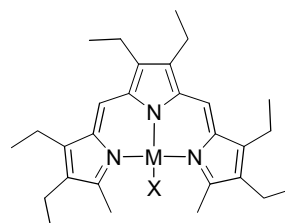


Fig.2. Structure of the tripyrrolic complexes. X represents an anion.

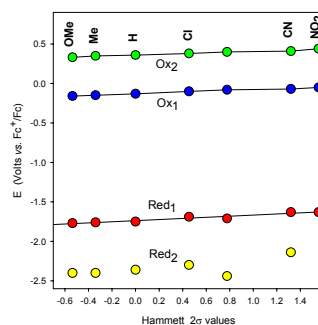
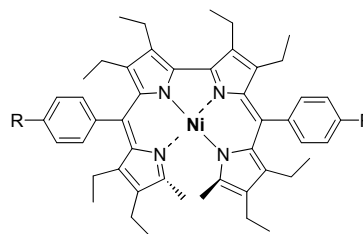


Fig. 3. Evolution of the redox potentials of a series of substituted Ni bidipyrin complexes versus the Hammett σ values of the R substituents.