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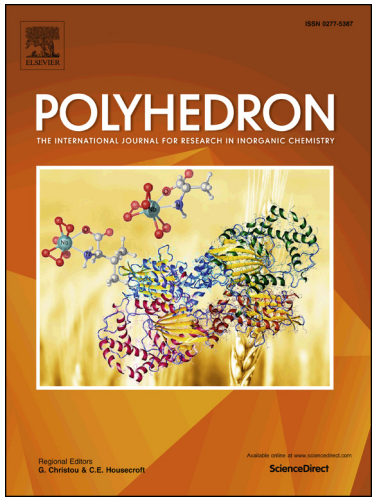

Synthesis, spectroscopic characterizations, cyclic voltammetry investigation and molecular structure of the high-spin manganese(III) trichloroacetato *meso*-tetraphenylporphyrin and *meso*-tetra-(*para*-bromophenyl)porphyrin complexes

Wafa Harhouri, Selma Dhifaoui, Zouhour Denden, Thierry Roisnel, Florent Blanchard, Habib Nasri

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Synthesis, spectroscopic characterizations, cyclic voltammetry investigation and molecular structure of the high-spin manganese(III) trichloroacetato *meso*-tetraphenylporphyrin and *meso*-tetra-(*para*-bromophenyl)porphyrin complexes

Wafa Harhouri[a]*, Selma Dhifaoui[a], Zouhour Denden[a], Thierry Roisnel[b], Florent Blanchard[c] and Habib Nasri[a]*

[a] *Laboratoire de Physico-chimie des Matériaux, University of Monastir, Faculté des Sciences de Monastir, Avenue de l'environnement, 5019 Monastir, Tunisia.*
[b] *Centre de Diffractométrie X, Institut des Sciences Chimiques de Rennes, UMR 6226, CNRS-Université de Rennes,1, Campus de Beaulieu, 35042 Rennes Cedex, France.*
[c] *ICSN Bât 27, 1 avenue de la Terrasse, 91190 Gif sur Yvette, France*

ABSTRACT

We present here the synthesis of two manganese(III) trichloroacetato porphyrins, namely (trichloroacetato)[5,10,15,20-tetraphenylporphyrinato]manganese(III) [Mn^{III}(TPP)(TCA)] (**1**) and (trichloroacetato)[(5,10,15,20-tetra-(*para*-bromophenyl)porphyrinato]manganese(III) hemi-chloroform hemi-dichloromethane solvates [Mn^{III}(TBrPP)(TCA)].1/2$CHCl_3$.1/2CH_2Cl_2 (**2**). These two new coordination compounds have been characterized by elemental analysis, UV-visible, IR and ^{1}H NMR spectroscopies, mass spectrometry, cyclic voltammetry and X-ray crystallography. The UV-visible spectra of **1** and **2** exhibit hyper type electronic spectra with very red shifted Soret bands, while the proton NMR spectra of these two Mn(III)-trichloroacetato metalloporphyrins present the β-pyrrole protons of the TPP and TBrPP porphyrinates as very upfield shifted bands, indicating that the two Mn(III) derivatives are high-spin (S = 2) with the ground state electronic configuration $(d_{xy}^1)(d_{xz,yz}^2)(d_{z^2}^1)$. The redox potential values of **1** and **2** are very close to each other and to other penta-coordinated high-spin Mn(III) metalloporphyrins. The average equatorial distance between the Mn cation and the nitrogen atoms of the porphyrin macrocycle (Mn—Np) of **1** and **2** are very close and are in the normal range for high-spin Mn(III) metalloporphyrins. The displacement of the manganese atom from the porphyrin mean plane (P_C) of the TBrPP derivative (**2**) is smaller than that of the TPP species (**1**) [0.147(1) and 0.236 (1) Å for **2** and **1** respectively], which is also the case for the deformations of the porphyrin core, where the TPP species (**1**) exhibits much higher *waving* and *saddle* deformations than the TBrPP derivative (**2**). Notably, the

* Corresponding author. Fax: +216 73 500 278.
E-mail address: hnasri1@gmail.com and habib.nasri@fsm.rnu.tn (Habib Nasri).

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