



# NOVEL $\mu$ -BRIDGED HETEROMETALLIC HETEROLEPTIC MACROCYCLIC TETRAPYRROLE COMPLEXES AS A MOLECULAR PLATFORM FOR CATALYSIS

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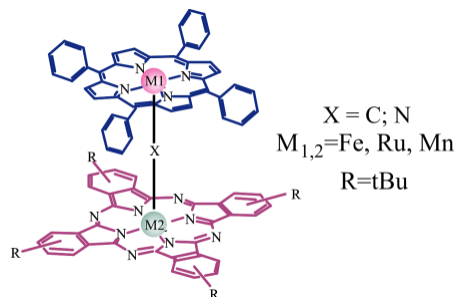
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## Abstract

Binuclear  $\mu$ -bridged complexes bearing porphyrin and phthalocyanine ligands and  $\text{Mn}^{\text{IV}}=\text{C}=\text{Ru}^{\text{IV}}$ ,  $\text{Fe}^{\text{IV}}=\text{C}=\text{Mn}^{\text{IV}}$ , or  $\text{Fe}^{\text{IV}}=\text{N}-\text{Mn}^{\text{III}}$  units were prepared and characterized for the first time. The compounds were identified by UV-Vis, IR and EPR spectroscopy, MALDI TOF mass spectrometry, as well as electrochemical techniques. The potential of the compounds obtained as oxidants for decomposing  $\beta$ -carotene upon exposure to  $t\text{BuOOH}$  was explored under mild conditions. The key intermediates were demonstrated to be stable and were detected spectrally.

**Key words:** mixed metal complexes, porphyrin and phthalocyanine ligands, room-temperature oxidation,  $\beta$ -carotene.



## Introduction

Versatility and importance of the active centers of enzymes, such as cytochrome p450, peroxidases, and methane monooxygenases, provoked an interest in the design of molecular platforms for catalysts capable of operating under mild conditions. An effective approach to the development of a simplified model of the active centers of enzymes is the use of dimeric X-bridged ( $X = \text{O}, \text{N}, \text{C}$ ) structures involving porphyrin-like macrocycles and transition metals, which are advantageous owing to high stability and several reaction centers (metal, ligand, bridging moiety). To date, such compounds have already found wide catalytic applications in various synthetic procedures, including oxidation of  $\beta$ -carotene, cyclopropanation of aromatic olefins, carbene insertion into N–H bonds of aromatic or aliphatic amines [1–5] and were even shown to be able to mediate methane oxidation [6, 7]. The incorporation of different metals or/and macrocyclic ligands and variation of the bridged atom in the dimer structures could offer the appealing opportunity for combining the advantages of various units and give valuable insights into the diverse effects of multiple components on the chemical reactivity, when they are placed in close proximity. As a result, tuning the desired properties through the selection of suitable constituent parts would be more efficient.

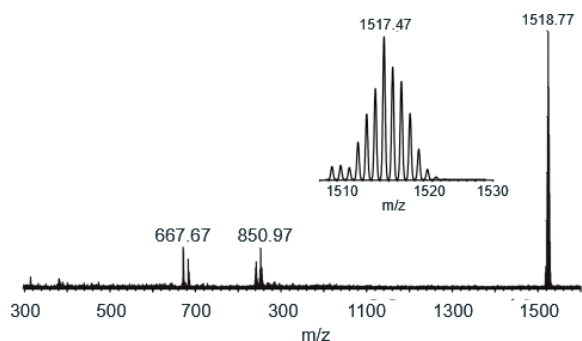
$\mu$ -Nitrido and  $\mu$ -carbido dimeric complexes with macrocyclic tetrapyrrole ligands are usually prepared according to the literature procedures [8, 9], which are also suitable for heterometallic heteroleptic analogs. However, investigations on the mixed metal heteroleptic complexes are limited to few reports [10–13]. The goal of this work was to expand this group of compounds.

## Results and discussion

In order to obtain new  $\mu$ -carbido heteroleptic complexes, we attempted the synthesis of  $\mu$ -carbido-[(tetra- $t\text{Bu}$ -phthalocyaninato)ruthenium(IV)]-(tetraphenylporphyrinato)-manganese(IV)]  $[\text{Bu}_4\text{PcRu}=\text{C}=\text{MnTPP}]$  (**1**) and  $\mu$ -carbido-[(tetra- $t\text{Bu}$ -phthalocyaninato)manganese(IV)]-(tetraphenylporphyrinato)iron(IV)]  $[\text{Bu}_4\text{PcMn}=\text{C}=\text{FeTPP}]$  (**2**), as well as  $\mu$ -nitrido-[(tetra- $t\text{Bu}$ -phthalocyaninato)manganese(III)]-(tetraphenylporphyrinato)iron(IV)]  $[\text{Bu}_4\text{PcMn}-\text{N}=\text{FeTPP}]$  (**3**). The detailed synthetic procedures, structures, full characterization data, and spectra of each of the compounds are presented in the Electronic supplementary information (ESI). Additionally, the redox activity of the dimers in the oxidation of  $\beta$ -carotene as an antioxidant was estimated.

First of all, the UV-Vis spectra of compounds **1–3** were not the same as the sum of the spectra of the initial monomers and contained absorbance assignable to both parts of the desired dimers (Figs. S1–S3 in the ESI). The dominant cluster peaks in the positive mode MALDI TOF spectra at  $m/z$  1517.77, 1472.34, and 1474.69, attributed to  $[\mathbf{1}]^+$ ,  $[\mathbf{2}]^+$ , and  $[\mathbf{3}]^+$ , respectively, confirmed the formation of dimers (Fig. 1 and Figs. S4, S5 in the ESI).

The IR spectra of the compounds showed the unique  $\mu$ -bridge marker bands at 983, 988, and 954  $\text{cm}^{-1}$ , which result from the  $\text{Ru}=\text{C}=\text{Mn}$ ,  $\text{Mn}=\text{C}=\text{Fe}$ , and  $\text{Mn}=\text{N}=\text{Fe}$  stretches, respectively (Fig. S6 in the ESI). While the oxidation state of metals in **1** and **2** is not in doubt and equal to +4, the metal centers in **3** are likely to have unbalanced charge distribution. The EPR studies of **3** in THF at 100 K ruled out  $\text{Mn}^{\text{IV}}$  ( $S = 3/2$ ;  $g \approx 4$ ) and  $\text{Fe}^{\text{III}}$  ( $S = 3/2$ ;  $g = 2.05, 6.0$ ) species due to the absence of the corresponding signals (Fig. S4 in the ESI). At the



**Figure 1.** MALDI TOF spectrum of  $^t\text{Bu}_4\text{PcRu}=\text{C}=\text{MnTPP}$  (**1**) in  $\text{CH}_2\text{Cl}_2$ .

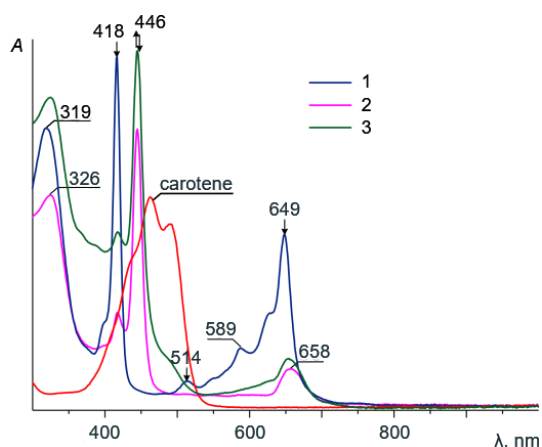
same time, the observed signal with an apparent hyperfine coupling pattern centered at  $g = 2$  for  $\text{Mn}^{\text{III}}$  ( $S = 2$ ) confirmed  $\text{Mn}^{\text{III}}-\text{N}=\text{Fe}^{\text{IV}}$  formulation for **3**.

The results of the cyclic voltammetric experiments summarized in Table 2 and Fig. S8 in the ESI revealed that, in the anodic region 0–1.5 V, all the studied compounds underwent three successive reversible oxidations typical for sequential oxidations of macrocycles.

**Table 1.** Oxidation half-wave potentials for the  $\mu$ -dimeric compounds ( $\text{CH}_2\text{Cl}_2$ , vs.  $\text{Ag}/\text{AgCl}$ )

Compound	$E_{1/2}$ , V		
	0/+	+2+	2+/3+
<b>1</b>	0.29	0.41	0.98
<b>2</b>	0.37	0.58	1.17
<b>3</b>	0.3	0.67	1.2

As the oxidized species of  $\mu$ -carbido and  $\mu$ -nitrido counterparts have been shown to be key intermediates competent for the oxidation of different organic substrates [1–7, 13], it was interesting to explore the possible catalytic applications of the novel  $\mu$ -carbido and  $\mu$ -nitrido dimers. Subjecting complexes **1–3** to  $^t\text{BuOOH}$  in  $\text{CH}_2\text{Cl}_2$  resulted in the chemical generation of high-valent species capable of mediating the  $\beta$ -carotene decomposition. The results of the interactions monitored by UV-Vis spectroscopy are presented in Fig. 2 and Figs. S9, S10 in the ESI.



**Figure 2.** UV-Vis spectra at 23 °C in  $\text{CH}_2\text{Cl}_2$ : **1** ( $C_1 = 1.95 \cdot 10^{-6}$  M) (**1**), **1**– $^t\text{BuOOH}$  system ( $C_{^t\text{BuOOH}} = 2.7 \cdot 10^{-3}$  M) in 5 min after mixing (**2**); **1**– $^t\text{BuOOH}$ – $\beta$ -carotene system ( $C_{\text{Car}} = 0.33$  mM) when mixed (**3**) with a carotene conversion of 99%.

Remarkably, the systems under study retained practically the same oxidative activity in the next several runs without any oxidant addition and the carotene degradation degree of about 99%, which indicated that the dimeric compounds are stable and can be recycled.

## Conclusions

Hence, it was shown that the newly synthesized  $\mu$ -bridged complexes might be attempted as suitable catalysts in substrate oxidations. Further work implies the investigations on the catalysis mechanism and the nature of active species. The synergistic effect of different metals, macrocyclic and bridging units in the dimers is of interest from the point of view of a detailed study of the structure–activity relationships. In general, the results of the performed work will expand the range of model compounds aiming at creating molecular platforms useful for practical applications.

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## Electronic supplementary information

Electronic supplementary information (ESI) available online: the synthetic procedures, the structures of the dimers, the UV-Vis, IR, EPR, and MALDI TOF spectra, cyclic voltammetry data. For ESI, see DOI: 10.32931/ioXXXXx.

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