

A Convenient Synthetic Route towards the Hybrid Binuclear Metallophthalocyaninato–Capped Iron and Nickel(II) Tris–pyridineoximates

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Earlier, the hybrid binuclear metallophthalocyaninato-capped iron and nickel(II) tris-pyridineoximates have been prepared using a two-step synthetic procedure via transmetalation reaction of their labile triethylantimony-capped precursors. We elaborated new efficient synthetic pathway to the preparation of the titled complexes. This synthetic approach is based on a one-pot template condensation of 2-acetylpyridinoxime with zirconium and hafnium(IV) phthalocyaninate on the corresponding metal ion(II) as a matrix, thus giving the target compounds in high yields (up to 83 %).

Keywords: Macrocyclic compounds, polynuclear complexes, template reaction, iron complexes, nickel complexes, phthalocyanines, zirconium complexes, hafnium complexes.

Удобный метод получения гибридных биядерных металлофталоцианинатовосодержащих трис–пиридиноксиматов железа и никеля(II)

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Ранее нами было описано получение гибридных биядерных металлофталоцианинато-сшитых трис-пиридиноксиматов железа и никеля(II) переметаллированием их сурьма-содержащих предшественников. Мы разработали новый эффективный синтетический путь для получения таких комплексов. Этот путь использует одностадийную темплатную конденсацию 2-ацетилпиридиноксима с фталоцианинатами циркония и гафния(IV) на матрице – ионе соответствующего металла(II), и позволяет получать искомые соединения с высокими выходами (до 83 %).

Ключевые слова: Макроциклические соединения, полиядерные комплексы, темплатная реакция, комплексы железа, комплексы никеля, фталоцианины, комплексы циркония, комплексы гафния.

Introduction

Cage metal complexes and their pseudomacrobicyclic analogs with an encapsulated metal ion (clathroche-

lates)^[1,2] are forms an individual class of the coordination compounds possessing unusual or, even, unique chemical reactivity, physical and physicochemical (including redox) properties.

Tetrapyrrole- (phthalocyaninate- or porphyrinate-) capped cage and pseudocage metal complexes belong to a subclass of hybrid clathrochelate-based compounds and several types of them with various (pseudo)encapsulated metal ions and different capping fragments have been synthesized to date.^[3-7] Recently,^[6] we reported a two-step synthetic approach (Scheme 1) that allowed to obtain the binuclear metallophthalocyaninate-capped metal(II) tris-pyridineoximates using a transmetallation of the initially obtained antimony-capped iron and nickel(II) tris-pyridineoximates with zirconium and hafnium(IV) phthalocyaninates as Lewis acids.

The transmetallation (a capping group exchange) reaction is a most common synthetic approach for the preparation of the hybrid cage metal complexes with tetrapyrrolic macroheterocyclic capping groups.^[3-7] However, the use of an extremely toxic triethylantimony(V) dibromide as a capping agent in this two-step procedure, thus allowing to isolate of the trialkylantimony-capped (pseudo-)clathrochelate complexes with labile capping groups, is its main disadvantage. In the present paper, we report an efficient antimony-free synthesis of the hybrid binuclear metallophthalocyaninate-capped iron and nickel(II) tris-pyridineoximates, allowing to obtain them in the moderate or, even high yields using their *one-pot* template self-assembly.

Experimental

The materials used and the details of the spectral experiments are described previously.^[6]

General procedure for the preparation of metal(IV) phthalocyaninate-capped iron and nickel(II) complexes. 2-Acetylpyridineoxime was dissolved in ethanol–chlorobenzene 2:3 (v/v) mixture (5 mL) and NaClO₄·H₂O, NaHCO₃, the corresponding metallophthalocyaninate {Zr(Cl₂)Pc or Hf(Cl₂)Pc} and the corresponding metal(II) salt {FeCl₂·4H₂O or Ni(ClO₄)₂·6H₂O} were added under argon. The reaction mixture was refluxed with stirring for 0.5 h. Then the reaction mixture was cooled to room temperature and the precipitate formed was filtered off, washed with ethanol (10 mL, in two portions), diethyl ether (5 mL) and dried *in vacuo* for 1 h. The solid product was extracted with dichloromethane (15 mL, in three portions), the extract was rotary evaporated to a small

volume (approximately 5 mL) and, then, it was purified by column chromatography on Al₂O₃ (eluent: chloroform – methanol 5: 1 (v/v) mixture). The major elute was collected, filtered and evaporated to dryness. The solid residue was washed with hexane and dried *in vacuo*.

[Fe(AcPyOx)₃(HfPc)](ClO₄). 2-Acetylpyridineoxime (0.057 g, 0.419 mmol), NaClO₄·H₂O (0.084 g, 0.599 mmol), NaHCO₃ (0.030 g, 0.359 mmol), Hf(Cl₂)Pc (0.101 g, 0.132 mmol) and FeCl₂·4H₂O (0.024g, 0.120 mmol) were used. The product was separated and purified as described above. Yield: 0.108 g (72 %).

[Fe(AcPyOx)₃(ZrPc)](ClO₄). 2-Acetylpyridineoxime (0.017 g, 0.123 mmol), NaClO₄·H₂O (0.015 g, 0.105 mmol), NaHCO₃ (0.009 g, 0.105 mmol), Zr(Cl₂)Pc (0.026 g, 0.39 mmol) and FeCl₂·4H₂O (0.007 g, 0.35 mmol) were used. The product was separated and purified as described above. Yield: 0.033 g (83 %).

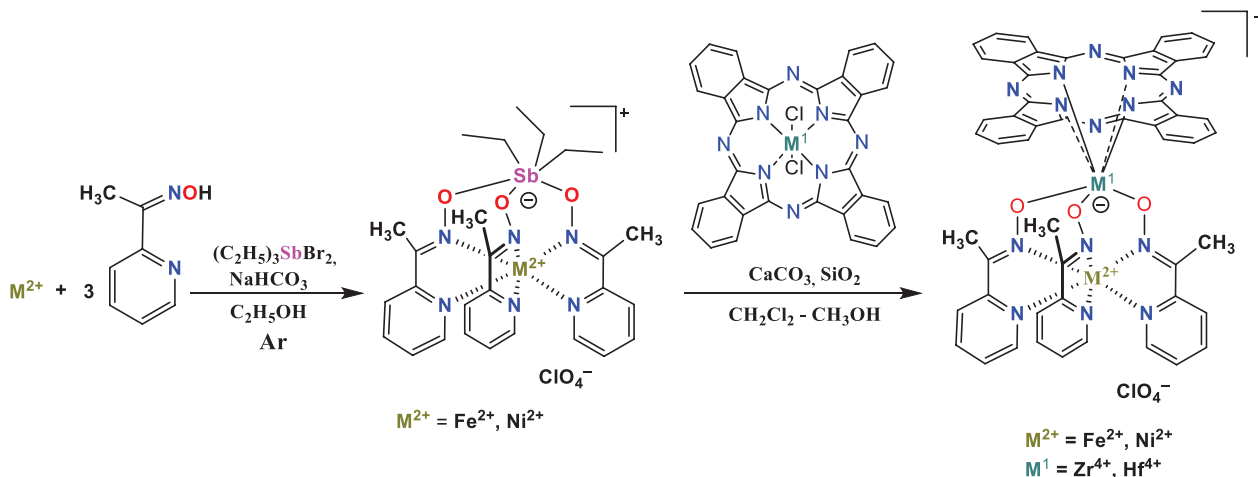
[Ni(AcPyOx)₃(HfPc)](ClO₄). 2-Acetylpyridineoxime (0.057 g, 0.419 mmol), NaClO₄·H₂O (0.034 g, 0.239 mmol), NaHCO₃ (0.020 g, 0.239 mmol), Hf(Cl₂)Pc (0.101 g, 0.132 mmol) and Ni(ClO₄)₂·6H₂O (0.044g, 0.120 mmol) were used. The product was separated and purified as described above. Yield: 0.098 g (65 %).

[Ni(AcPyOx)₃(ZrPc)](ClO₄). 2-Acetylpyridineoxime (0.016 g, 0.119 mmol), NaClO₄·H₂O (0.014 g, 0.102 mmol), NaHCO₃ (0.009 g, 0.102 mmol), Zr(Cl₂)Pc (0.025 g, 0.37 mmol) and Ni(ClO₄)₂·6H₂O (0.012 g, 0.34 mmol) were used. The product was separated and purified as described above. Yield: 0.027 g (68 %).

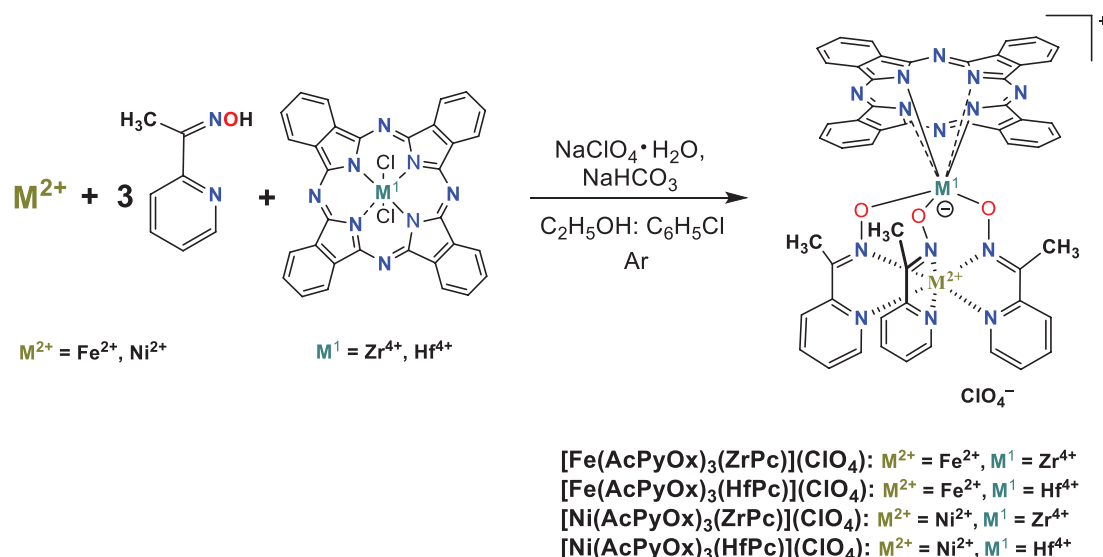
Results and Discussion

The hybrid binuclear metallophthalocyaninate-capped complexes under study were obtained in the yields from moderate to high (Table 1) by Scheme 2 using the direct template condensation of 2-acetylpyridineoxime with an equimolar amount of the Lewis-acidic zirconium or hafnium(IV) phthalocyaninates on the corresponding metal ion(II) as a matrix.

A formation of the known^[6] metallophthalocyaninate-capped tris-pyridineoximates was confirmed by elemental analysis, 1D (¹H and ¹³C{¹H}) and 2D NMR, MALDI-TOF MS data, as well as using their UV-Vis spectra (Figure 1). All the spectral data for these isolated complexes were identical to those described previously.^[6]



Scheme 1.



Scheme 2.

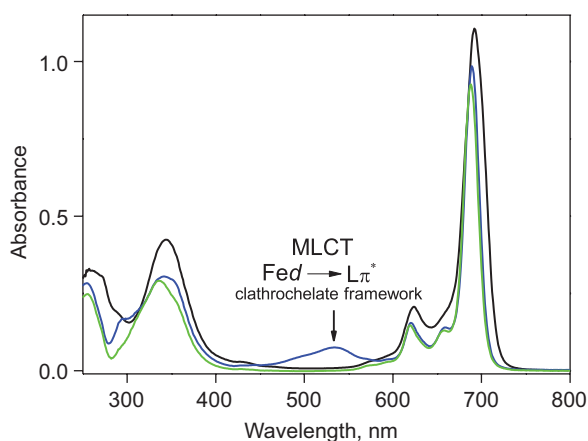


Figure 1. UV-Vis spectrum of a DMSO solution of the parent $Hf(Cl_2)_2Pc$ (black) and that of its derivatives $[Fe(AcPyOx)_3(HfPc)](ClO_4)$ (blue) and $[Ni(AcPyOx)_3(HfPc)](ClO_4)$ (green) in CH_2Cl_2 .

Conclusions

We elaborated a new direct synthetic approach for preparation of the hybrid binuclear metallophthalocyaninato-capped iron and nickel(II) tris-pyridineoximates using the *one-pot* reaction giving them in the yields from moderate to high. This allows to avoid the initial isolation of their antimony-capped precursors and, therefore, the use of the toxic trialkylantimony derivatives.

Acknowledgements. The synthesis of the hybrid complexes was supported by the Russian Science Foundation (project 16-13-10475). Their spectral characterization was performed with the financial support from the Russian Foundation for Basic Research (projects 16-03-00368 and 17-03-00587).

Table 1. The isolated yields of the metallophthalocyaninato-capped tris-pyridineoximates, which were obtained using a direct self-assembly and by a transmetallation reaction.

	Yield, %	
	One-pot reaction	Trans-metallation ^[6]
$[Fe(AcPyOx)_3(ZrPc)](ClO_4)$	83	39
$[Fe(AcPyOx)_3(HfPc)](ClO_4)$	72	42
$[Ni(AcPyOx)_3(ZrPc)](ClO_4)$	68	50
$[Ni(AcPyOx)_3(HfPc)](ClO_4)$	65	46

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Received 10.10.2018

Accepted 28.12.2018