Макрогетероциклы
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DOI: 10.6060/mhc190550d

Pseudomacrobicyclic Phthalocyaninate–Capped Cobalt(III) tris–Pyridineoximates: Template Synthesis, X–Ray Structure and Spectral Characteristics

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First pseudomacrobicyclic phthalocyaninate-capped cobalt(III) tris-pyridineoximates were obtained in moderate yields (40–49 %) by the direct template condensation of 2-acetylpyridineoxime with zirconium(IV) and hafnium(IV) phthalocyaninates on the cobalt ion as a matrix. These complexes were thoroughly characterized using elemental analysis, MALDI-TOF mass-spectrometry, NMR and UV-Vis spectroscopies and by the single-crystal X-ray diffraction. Their electrochemical behaviour was studied byusing the cyclic and differential pulse voltammetries.

Keywords: Macrocyclic compounds, phthalocyanines, polynuclear complexes, template reactions, cobalt complexes, zirconium complexes, hafnium complexes.

Псевдомакробициклические фталоцианинато–сшитые трис–пиридиноксиматы кобальта(III): получение, структура и спектральные характеристики

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Первые псевдомакробициклические фталоцианинато-сшитые трис-пиридиноксиматы кобальта(III) получены с умеренными выходами (40–49 %) темплатной конденсацией 2-ацетилпиридиноксима с фталоцианинатами циркония(IV) и гафния(IV) на матрице – ионе кобальта. Полученные комплексы охарактеризованы методами элементного анализа, MALDI-TOF масс-спектрометрии, ЯМР и оптической спектроскопии, а также рентгеноструктурного анализа. Их электрохимические свойства изучены методами циклической и дифференциальной импульсной вольтамперометрии.

Ключевые слова: Макроциклические соединения, фталоцианины, полиядерные комплексы, темплатные реакции, комплексы кобальта, комплексы циркония, комплексы гафния.

Introduction

First representatives of a new type of the coordination compounds, the hybrid tetrapyrrole-clathrochelates with porphyrinate or phthalocyaninate fragment(s) in their apical fragment(s), have been recently prepared.[1,2] In these complexes, the tetrapyrrolic macrocycle(s) and the clathrochelate framework are quasi-isolated, so that each of them can be individually functionalized in several positions using a wide range of various substituents (including the reactive ones).[3-6] They have been synthesized[1,2,7-9] by transmetallation of their reactive antimony-capped clathrochelate precursors using a Lewis acidity of the appropriate metal tetrapyrroles. However, the kinetically inert bis-triethylantimony-capped cobalt(III) clathrochelates did not undergo this reaction. Therefore, a successful application of the above synthetic approach relies on a wise choice of a template ion and the lability and reactivity of the antimony-capped (pseudo)clathrochelate precursors. In particular,[8] we have succeeded in the praparation of the reactive monoantimony-capped iron and nickel(II) pseudoclathrochelates but failed to obtain their cobalt(II)-containing analogs.

Recently,[10] we have developed an easy and convenient synthetic pathway towards the binuclear metallophthalocyaninato-capped iron and nickel(II) tris-pyridineoximates that produces them in high yields using the direct template condensation of the appropriate ligand synthons on the corresponding metal(II) ion. Here we report the results of our efforts to extend this synthetic approach for the preparation of hybrid metallo(IV)phthalocyaninate-capped cobalt(III) tris-pyridineoximates.

Experimental

The reagents used, $NaClO_4 \cdot H_2O$, $NaHCO_3$, 2-acetylpyridine, sorbents and solvents were obtained commercially (SAF). The zirconium(IV) and hafnium(IV) phthalocyaninates **Zr(Cl$_2$)Pc** and **Hf(Cl$_2$)Pc**,[11] 2-acetylpyridineoxime[12] and $Co(ClO_4)_2 \cdot 6H_2O$[13] have been prepared as described elsewhere.

Analytical data for C, H, N contents were obtained with a Carlo Erba model 1106 microanalyzer. MALDI-TOF mass spectra were recorded in the positive and negative ranges with a MALDI-TOF-MS Bruker Autoflex II (Bruker Daltonics) mass spectrometer in a reflecto-mol mode. The ionization was induced by an UV-laser with the wavelength of 337 nm. The samples were applied to a nickel plate, and 2,5-dihydroxybenzoic acid was used as the matrix. The accuracy of measurements was 0.1 %. UV-Vis spectra were recorded from acetonitrile or DMSO solutions in the range 250–800 nm with a Varian Cary 50 spectrophotometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded in CD_3CN solutions with a Bruker Avance 600 spectrometer. The measurements were done using the residual signals of CD_3CN (^{1}H 1.94 ppm, ^{13}C 1.32 and 118.26 ppm). Data acquisition and processing were performed with Topspin 2.1 and Mestrenova 9.0.0 software, respectively. CV and DPV experiments were performed for dichloromethane solutions with 0.1 M (n-$(C_4H_9)_4N)PF_6$ as a supporting electrolyte using a Metrohm Autolab PGSTAT128N potentiostat with a conventional one-compartment three-electrode cell (5 ml of solution). A platinum wire counter electrode and standard Ag/AgCl/NaCl$_{aq.}$ reference electrode (RE-5B, BASi) were used. Platinum disk electrode (MF-2013, BASi, d = 1.6 mm) or glassy carbon disk electrode (MF-2012, BASi, d = 3.0 mm), which were used as a working electrode, was thoroughly polished with 0.05 µm alumina slurry, sonicated for 2 min in deionized water and rinsed before every measurement. The solutions were thoroughly deaerated by passing argon stream through them before the CV and DPV experiments and above these solutions during the experiments.

General synthetic procedure for preparation of the metal(IV) phthalocyaninate-capped cobalt(III) tris-pyridineoximates. 2-Acetylpyridineoxime was dissolved in ethanol – chlorobenzene 2:3 (v/v) mixture (5 mL), and $NaClO_4 \cdot H_2O$, $NaHCO_3$, the corresponding metallophthalocyaninate {**Zr(Cl$_2$)Pc** or **Hf(Cl$_2$)Pc**} and $Co(ClO_4)_2 \cdot 6H_2O$ were added under argon. The reaction mixture was refluxed and then cooled to ambient temperature. The precipitate formed was filtered off, washed with chlorobenzene (2×2 mL), ethanol (3×5 mL) and diethyl ether (7 mL) and then dried *in vacuo*. The solid product was extracted with dichloromethane (7×7 mL) and acetonitrile (2×5 mL), the extracts were combined and rotary evaporated to a small volume (approximately 5 mL). Then the product was purified using column chromatography on Al_2O_3 (eluents: chloroform and then acetonitrile). The major bluish elute was collected and evaporated to dryness. The solid residue was washed with hexane and dried *in vacuo*.

[Co(AcPyOx)$_3$(ZrPc)](ClO$_4$)$_2$. 2-Acetylpyridineoxime (0.016 g, 0.117 mmol), $NaClO_4 \cdot H_2O$ (0.014 g, 0.099 mmol), $NaHCO_3$ (0.009 g, 0.107 mmol), Zr(Cl$_2$)Pc (0.025 g, 0.037 mmol) and $Co(ClO_4)_2 \cdot 6H_2O$ (0.012 g, 0.033 mmol) were used. The product was separated and purified as described above. Yield: 0.016 g (40 %). Found: C 50.04, H 3.05, N 15.59 %. Calculated for $C_{53}H_{37}N_{14}O_{11}Cl_2CoZr$: C 50.24, H 2.94, N 15.48 %. *m/z* (MALDI-TOF) 1066.1088 [MCo(II)-ClO$_4$]$^+$. UV-Vis (acetonitrile) λ_{max} (lgε) nm: 333 (4.48), 356sh (4.78), 622 (4.53), 659sh (4.51), 690 (5.29). ^{1}H NMR (CD_3CN) δ_H ppm: 0.52 (s, 9H, CH$_3$), 5.57 (d, 3H, 6-Py), 6.87 (m, 3H, 5-Py), 7.05 (d, 3H, 3-Py), 7.69 (m, 3H, 4-Py), 8.42 (m, 8H, β-Pc), 8.99 (m, 8H, α-Pc). ^{13}C NMR (CD_3CN) δ_C ppm: 11.30 (s, CH$_3$), 123.44 (d, α-Pc), 126.00 (s, 3-Py), 128.05 (s, 5-Py), 131.70 (d, β-Pc), 135.65 (d, C(Pc)), 141.82 (s, 4-Py), 149.95 (s, 6-Py), 151.80 (s, C=N(Pc)), 151.86 (s, C=N(Pc)), 153.58 (s, 2-Py), 159.43 (s, C=N).

[Co(AcPyOx)$_3$(HfPc)](ClO$_4$)$_2$. 2-Acetylpyridineoxime (0.057 g, 0.419 mmol), $NaClO_4 \cdot H_2O$ (0.034 g, 0.242 mmol), $NaHCO_3$ (0.020 g, 0.238 mmol), Hf(Cl$_2$)Pc (0.100 g, 0.131 mmol) and $Co(ClO_4)_2 \cdot 6H_2O$ (0.044 g, 0.120 mmol) were used. The product was separated and purified as described above. Yield: 0.073 g (49 %). Found: C 47.04, H 2.90, N 14.67 %. Calculated for $C_{53}H_{37}N_{14}O_{11}Cl_2CoHf$: C 47.00, H 2.75, N 14.48 %. *m/z* (MALDI-TOF) 1156.4839 [MCo(II)-ClO$_4$]$^+$. UV-Vis (acetonitrile) λ_{max} (lgε) nm: 331 (4.87), 367sh (4.60, 621 (4.52), 655sh (4.50), 689 (5.29). ^{1}H NMR (CD_3CN) δ_H ppm: 0.55 (s, 9H, CH$_3$), 5.53 (d, 3H, 6-Py), 6.86 (m, 3H, 5-Py), 7.04 (d, 3H, 3-Py), 7.69 (m, 3H, 4-Py), 8.43 (m, 8H, β-Pc), 9.01 (m, 8H, α-Pc). ^{13}C NMR (CD_3CN) δ_C ppm: 11.28 (s, CH$_3$), 123.45 (d, α-Pc), 125.96 (s, 3-Py), 128.06 (s, 5-Py), 131.73 (d, β-Pc), 135.78 (d, C(Pc)), 141.78 (s, 4-Py), 149.90 (s, 6-Py), 155.15 (s, C=N(Pc)), 155.21 (s, C=N(Pc)), 153.49 (s, 2-Py), 160.08 (s, C=N).

X-Ray diffraction data for **[Co(AcPyOx)$_3$(ZrPc)](ClO$_4$)$_2$** were collected at the protein station of Kurchatov Centre for Synchrotron radiation (λ = 0.9699 Å) at 100 K. The structure was solved by the direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. Positions of hydrogen atoms were calculated, and they were refined in the isotropic approximation within the riding model. All the calculations were performed with the SHELXTL program package.[14] Crystal data and structure refinement parameters are given in Table 1. CCDC 1912219 contains the supplementary crystallographic information.

Results and Discussion

Synthesis

The complexes **[Co(AcPyOx)$_3$(ZrPc)](ClO$_4$)$_2$** and **[Co(AcPyOx)$_3$(HfPc)](ClO$_4$)$_2$** were obtained using

Table 1. Crystal data and structure refinement parameters for **[Co(AcPyOx)$_3$(ZrPc)](ClO$_4$)$_2$**.

Empirical formula	$C_{56}H_{43}Cl_8CoN_{14}O_{11}Zr$
Formula weight	1521.83
Crystal system	Triclinic
Space group	*P-1*
Z	2
a, Å	13.437(3)
b, Å	15.516(3)
c, Å	15.546(3)
α, °	103.54(3)
β, °	102.87(3)
γ, °	95.82(3)
V, Å^3	3031.4(13)
D_{calc} (g cm^{-1})	1.667
Linear absorption, μ (cm^{-1})	21.52
F(000)	1539
$2\theta_{max}$, °	71
Reflections measured	30057
Independent reflections	10611
Observed reflections [$I > 2\sigma(I)$]	6863
Parameters	786
R1	0.1007
wR2	0.2797
GOF	0.951
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	4.693/-3.609

the direct template condensation of 2-acetylpyridineoxime with an equimolar amount of zirconium(IV) or hafnium(IV) phthalocyaninate on the cobalt(II) ion as a matrix (Scheme 1). However, the isolated products were the hybrid metallo(IV)phthalocyaninate-capped cobalt(III) complexes that resulted from an oxidation Co(II) → Co(III) occurring even in an argon atmosphere; the same Co(II) → Co(III) oxidation process has been earlier observed under the conditions of analogous template reaction.[15-17]

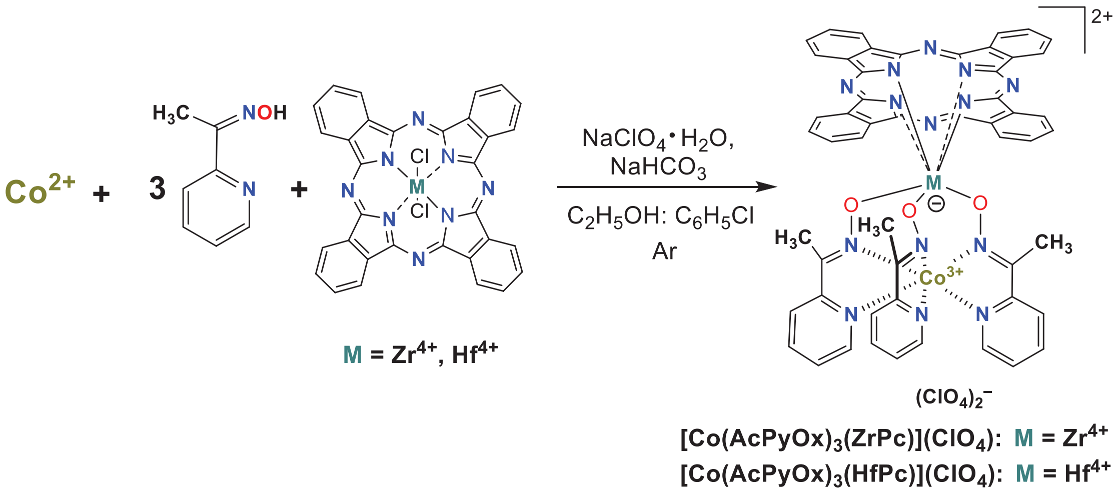
These new metallo(IV)phthalocyaninate-capped cobalt(III) tris-pyridineoximates were thoroughly characterized using elemental analysis, MALDI-TOF mass-spectrometry, NMR and UV-Vis spectroscopies and by the single-crystal X-ray diffraction. Their electrochemical behaviour was studied using cyclic (CV) and differential pulse (DPV) voltammetries.

NMR Spectroscopy

As the low-spin *d*^{6} electronic configuration of the cobalt(III)-containing hybrid complexes **[Co(AcPyOx)$_3$(ZrPc)](ClO$_4$)$_2$** and **[Co(AcPyOx)$_3$(HfPc)](ClO$_4$)$_2$** is the same as that in their earlier reported[8] iron(II)-containing analogues, the NMR spectra of these complexes are essentially the same. However, the difference in a redistribution of electron density due to the nature of the encapsulated ion causes a sligt shift of the signals for the majority of protons (except for those of the methyl groups) in the cobalt(III) complexes towards the low-field region as compared to their iron(II)-containing analogues.

UV-Vis Spectroscopy

UV-Vis spectra of the hybrid complexes **[Co(AcPyOx)$_3$(ZrPc)](ClO$_4$)$_2$** and **[Co(AcPyOx)$_3$(HfPc)](ClO$_4$)$_2$** measured in their acetonitrile solutions at room temperature are shown in Figure 1. They are very similar to each other and to those of the initial metallo(IV)phthalocyaninates. These spectra are dominated by very intensive absorption bands of the corresponding metallo(IV) phthalocyaninate fragments, preventing the observation of other bands typical for cobalt(III) tris-dioximates. The latter include low-intensive *d–d* bands of the cobalt(III) ion in its low-spin state and more intensive metal-to-ligand charge transfer (MLCT) Co $d \rightarrow L_{\pi*}$ bands. The UV-Vis spectra of **[Co(AcPyOx)$_3$(ZrPc)](ClO$_4$)$_2$** and **[Co(AcPyOx)$_3$(HfPc)](ClO$_4$)$_2$** also contain a very



Scheme 1.

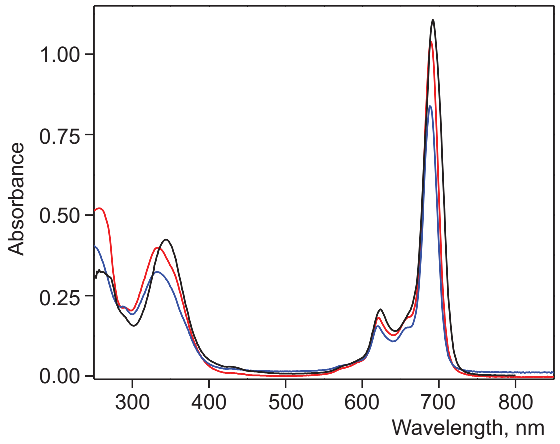


Figure 1. UV-Vis spectra of **[Co(AcPyOx)$_3$(HfPc)](ClO$_4$)$_2$** (in red) and **[Co(AcPyOx)$_3$(ZrPc)](ClO$_4$)$_2$** (in blue) in acetonitrile and of a parent complex **Hf(Cl$_2$)Pc** in DMSO (in black).

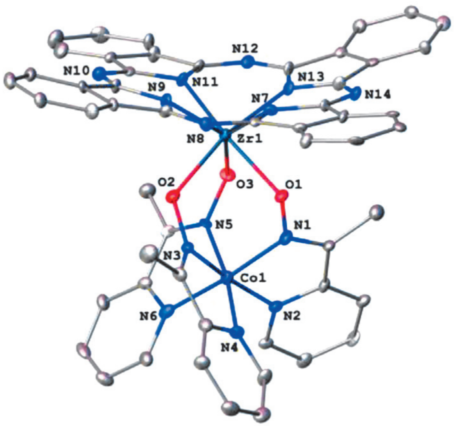


Figure 2. General view of the dication **[Co(AcPyOx)$_3$(ZrPc)]$^{2+}$** with atoms shown as thermal ellipsoids at 30 % probability level. Hydrogen atoms, perchlorate anions and solvate dichloromethane molecules are omitted for clarity.

intensive *Q* band (at ~690 nm) and its vibronic satellites (at 621 and 655 nm), which are characteristic for a Pc core. The corresponding *B* band in the near-UV range is slightly broadened due to the presence of cobalt(III)-containing tris-pyridineoximate fragment.

X-Ray Diffraction

The structure of the hybrid cobalt(III) complexes has been confirmed by X-ray diffraction analysis (Figure 2) of **[Co(AcPyOx)$_3$(ZrPc)](ClO$_4$)$_2$** obtained with three lattice molecules of dichloromethane. The CoN$_6$ polyhedron adopts a geometry that is much closer to a trigonal antiprism (TAP, φ = 60°) than to a trigonal prism (TP, the distortion angle φ = 0°); the corresponding distortion angle φ is 49.2(2)°. This distortion is nearly the same as in the previously reported zirconium-capped low-spin iron(II) and high-spin nickel(II) pseudoclathrochelates (with φ equal to 46.4 and 37.8°, respectively).[8] With only one capping fragment in **[Co(AcPyOx)$_3$(ZrPc)](ClO$_4$)$_2$**, its CoN$_6$ polyhedron can be alternatively described as a truncated trigonal pyramid (Co–N 1.896(6)–1.962(6) Å). The encapsulated metal ion is located almost in its center, as typical for low-spin cobalt(III) ion, and is only slightly shifted along the Co···Zr line.

The capping zirconium(IV) ion coordinates three oxygen atoms of the caging ligand (Zr–O 2.138(5)–2.217(5) Å) and four nitrogen atoms of the phthalocyaninate core (Zr–N 2.220(6)–2.251(5) Å), as in the above iron(II) and nickel(II) pseudoclathrochelates.[8] In all these cases, the zirconium(IV) ion is displaced by ~1.1 Å from the plane of the four nitrogen atoms of the phthalocyaninate core, which itself has a dome-like geometry. Stacking interactions between these cores produce “base-to-base” dimer as a main supramolecular motif in **[Co(AcPyOx)$_3$(ZrPc)](ClO$_4$)$_2$**.

Electrochemistry

The redox behaviour of the hybrid cobalt(III) complexes was studied by cyclic (CV) and differential pulse (DPV) voltammetries for a dichloromethane/(n-(C$_4$H$_9$)$_4$N)PF$_6$ solution of **[Co(AcPyOx)$_3$(ZrPc)](ClO$_4$)$_2$**. The obtained CV and DPV data (Figures 3 and 4) showed one oxidation and one reduction wave at the potentials of −0.27 and 1.01 V, respectively. They are quasi-reversible, as follows from ΔE_p values that fall in the range of 70–80 mV and from the current ratio for direct and reverse processes that is close to 1. Irreversible redox processes are also observed outside of the region shown in Figure 3. The resolution is slightly improved by applying DPV and substituting the platinum working electrode with a glassy carbon electrode (Figure 4), which results in two additional reduction processes detected at −0.75 and −0.95 V.

These potentials, as well as the potential for the oxidation process at 1.01 V, are very close to one observed earlier for phthalocyanine-capped (pseudo)clathrochelates[8,18] and zirconium(IV) phthalocyanines with β-diketone axial ligands,[19] allowing us to assign it to a phthalocyanine-centered process. However, the reduction at −0.27 V is not characteristic for such hybrid complexes and was therefore

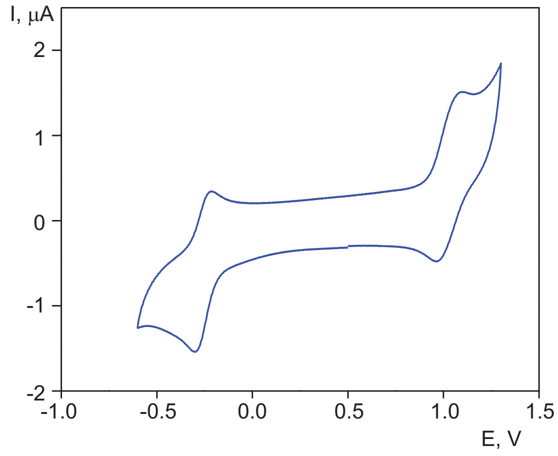


Figure 3. CV curve for 0.1 mM dichloromethane solution of **[Co(AcPyOx)$_3$(ZrPc)](ClO$_4$)$_2$** with 0.1 M (n-(C$_4$H$_9$)$_4$N)PF$_6$ as a supporting electrolyte. Conditions: scan rate 100 mV s^{-1}, 298 K, platinum working and counter electrodes; the potentials are referenced to Ag/AgCl.

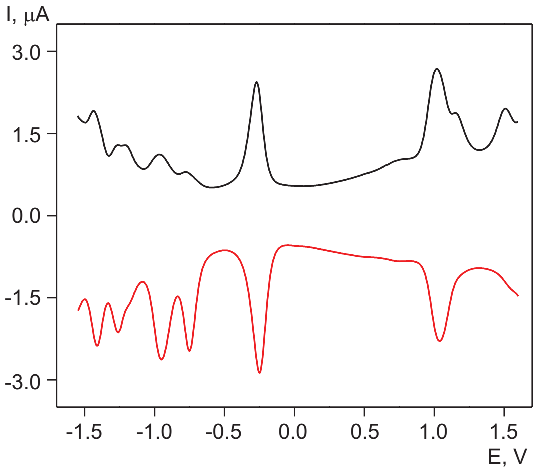


Figure 4. DPV curve for 0.1 mM dichloromethane solution of **$[Co(AcPyOx)_3(ZrPc)](ClO_4)_2$** with 0.1 M $(n\text{-}(C_4H_9)_4N)PF_6$ as a supporting electrolyte. Conditions: scan rate 100 mV s^{-1}, 298 K, glassy carbon working and platinum counter electrodes; the potentials are referenced to Ag/AgCl.

assigned to a redox pair Co^{3+}/Co^{2+}. The relatively low potential for this process is, apparently, behind the stabilization of the cobalt ion in the oxidation state +3 in the obtained phthalocyanine-capped cobalt pseudoclathrochelates **$[Co(AcPyOx)_3(ZrPc)](ClO_4)_2$** and **$[Co(AcPyOx)_3(HfPc)](ClO_4)_2$** in contrast to similar iron(II) and nickel(II) complexes.[8]

Conclusions

One-step synthetic approach allowed to obtain two new phthalocyaninate-capped cobalt(III) pseudoclathrochelates in moderate yields by direct template condensation of 2-acetylpyridineoxime with zirconium(IV) and hafnium(IV) phthalocyaninates on the cobalt(II) ion as a matrix. The obtained cobalt(III) complexes, which resulted from an oxidation Co(II) → Co(III) occurring even in argon atmosphere, were thoroughly characterized using various methods (including the single crystal XRD). Their electrochemical behaviour was studied by cyclic and differential pulse voltammetries.

Acknowledgements. The synthesis of the hybrid complexes and their characterization by NMR, X-ray diffraction and electrochemistry were supported by Russian Science Foundation (Project 17-73-20369). Elemental analysis was performed at the Center for molecular composition studies of INEOS RAS with a financial support from Ministry of Science and Higher Education of the Russian Federation. MALDI-TOF mass spectrometric measurements were performed using the equipment of CKP FMI IPCE RAS. UV-Vis spectra collection was supported by Russian Foundation for Basic Research (Projects 19-03-00357, 17-03-00587 and 18-29-23007). YZV also thanks the EU Research and Innovation Staff Exchange (RISE) program (H2020-MSCA-RISE-2017, Project 778245 'CLATHROPROBES') for partially covering travel expenses and IGIC RAS state assigment.

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Received 05.05.2019
Accepted 15.05.2019