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

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First pseudomacroyclic 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 by using the cyclic and differential pulse voltammetries.

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

Pсевдомакробициклические 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 фталоцианинами циркония(IV) и гафния(IV) на матрице – ион 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 tetrapyrole-clathrochelates with porphyrinate or phthalocyaninate fragment(s) in their apical fragment(s), have been recently prepared.[1-2] In these complexes, the tetrapyrole 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). They have been synthesized[2,3-9] by transmetallation of their reactive antimony-capped clathrochelate precursors using a Lewis acidity of the appropriate metal tetrapyroles. 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 reaction. Therefore, a successful application of the above synthetic approach for the preparation of hybrid metallo(IV)phthalocyaninate-capped cobalt(III) tris-pyridineoximates. Here we report the results of our condensation of the appropriate ligand synthons on the corresponding metal(II) ion. In particular, we have succeeded in the preparation 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, NaClO4·H2O, NaHCO3, 2-acetylpyridineoxime, sorbents and solvents were obtained commercially (SAF). The zirconium(IV) and hafnium(IV) phthalocyaninates Zr(Cl2)Pc and Hf(Cl2)Pc[11,12] and ZrCl3·6H2O[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 samples were applied to a nickel plate, and 2,5-dihydroxybenzoic acid was used as the matrix. The samples were applied to a nickel plate, and 2,5-dihydroxybenzoic acid was used as the matrix. The samples were applied to a nickel plate, and 2,5-dihydroxybenzoic acid was used as the matrix.

X-Ray diffraction data for [Co(AcPyOx)3(ZrPe)](ClO4)2 were collected at the protein station of Kurchatov Centre for Synchrotron radiation (λ=0.9969 Å) at 100 K. The structure was solved by the direct method and refined by the full-matrix least-squares technique against F2 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(ZrPe)](ClO4)2 and [Co(AcPyOx)3(HfPe)](ClO4)2 were obtained using 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-Acetylpyridineoxide was dissolved in ethanol – chlorobenzene 2:3 (v/v) mixture (5 mL), and NaClO4·H2O, NaHCO3, the corresponding metallophthalocyaninato Zr(Cl2)Pc or Hf(Cl2)Pc and Co(ClO4)2·6H2O 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 acetoneitrile (2+5 mL), the extracts were combined and rotated evaporated to a small volume (approximately 5 mL). Then the product was purified using column chromatography on Al2O3 (eluents: chloroform and then acetoneitrile). The major bluish eluate was collected and evaporated to dryness. The solid residue was washed with hexane and dried in vacuo.

\[\text{[Co(AcPyOx)3(ZrPe)](ClO4)2} \]

2-Acetylpyridineoxide (0.016 g, 0.117 mmol), NaClO4·H2O (0.014 g, 0.099 mmol), NaHCO3 (0.009 g, 0.107 mmol), Zr(Cl2)Pc (0.025 g, 0.037 mmol) and Co(ClO4)2·6H2O (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 C53H37N14O10: C 50.61, H 3.00, N 14.63 %.

\[\text{[Co(AcPyOx)3(HfPe)](ClO4)2} \]

2-Acetylpyridineoxide (0.057 g, 0.419 mmol), NaClO4·H2O (0.034 g, 0.242 mmol), NaHCO3 (0.020 g, 0.238 mmol), Hf(Cl2)Pc (0.100 g, 0.131 mmol), and Co(ClO4)2·6H2O (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 C53H37N14O10: C 47.93, H 2.93, N 14.67 %.

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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 $[\text{Co(AcPyOx)}_3(\text{ZrPc})](\text{ClO}_4)_2$ and $[\text{Co(AcPyOx)}_3(\text{HfPc})](\text{ClO}_4)_2$ is the same as that in their earlier reported[9] 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 slight 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 $[\text{Co(AcPyOx)}_3(\text{ZrPc})](\text{ClO}_4)_2$ and $[\text{Co(AcPyOx)}_3(\text{HfPc})](\text{ClO}_4)_2$ 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) $\text{Co}^2+\rightarrow\lambda^-(\pi^*)$ bands.

The UV-Vis spectra of $[\text{Co(AcPyOx)}_3(\text{ZrPc})](\text{ClO}_4)_2$ and $[\text{Co(AcPyOx)}_3(\text{HfPc})](\text{ClO}_4)_2$ also contain a very the direct template condensation of 2-acetylpyridine-oxime 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]

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The UV-Vis spectra of $[\text{Co(AcPyOx)}_3(\text{ZrPc})](\text{ClO}_4)_2$ and $[\text{Co(AcPyOx)}_3(\text{HfPc})](\text{ClO}_4)_2$ also contain a very

| Table 1. Crystal data and structure refinement parameters for $[\text{Co(AcPyOx)}_3(\text{ZrPc})](\text{ClO}_4)_2$. |
|-----------------|-----------------|
| **Empirical formula** | $\text{C}_{56}\text{H}_{43}\text{Cl}\text{N}_{14}\text{O}_{11}\text{Zr}$ |
| **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) |
| **$\alpha$, °** | 103.54(3) |
| **$\beta$, °** | 102.87(3) |
| **$\gamma$, °** | 95.82(3) |
| **$V$, Å$^3$** | 3031.4(13) |
| **$D_{\text{calc}}$, (g cm$^{-1}$)** | 1.667 |
| **Linear absorption, $\mu$, (cm$^{-1}$)** | 21.52 |
| **$F(000)$** | 1539 |
| **$2\theta_{\text{max}}$, °** | 71 |
| **Reflections measured** | 30057 |
| **Independent reflections** | 10611 |
| **Observed reflections** | 6863 |
| **Parameters** | 786 |
| **$R_1$** | 0.1007 |
| **$wR_2$** | 0.2797 |
| **GOF** | 0.951 |
| **$\Delta \rho_{\text{max}}/\Delta \rho_{\text{min}}$, (e Å$^{-3}$)** | 4.693/-3.609 |
Phthalocyaninate-Capped Cobalt(III) tris-Pyridineoximates

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

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 \([\text{Co}(\text{AcPyOx})_3(\text{ZrPc})](\text{ClO}_4)_2\) obtained with three lattice molecules of dichloromethane. The \(\text{CoN}_6\) polyhedron adopts a geometry that is much closer to a trigonal antiprism (TAP, \(\varphi = 60^\circ\)) than to a trigonal prism (TP, the distortion angle \(\varphi = 0^\circ\)); the corresponding distortion angle \(\varphi\) 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 \(\varphi\) equal to 46.4 and 37.8°, respectively).[8] With only one capping fragment in \([\text{Co}(\text{AcPyOx})_3(\text{ZrPc})](\text{ClO}_4)_2\), its \(\text{CoN}_6\) 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 \([\text{Co}(\text{AcPyOx})_3(\text{ZrPc})](\text{ClO}_4)_2\).

**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 \([\text{Co}(\text{AcPyOx})_3(\text{ZrPc})](\text{ClO}_4)_2\). 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 \(\Delta E_p\) 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 2.** General view of the dication \([\text{Co}(\text{AcPyOx})_3(\text{ZrPc})]^2+\) with atoms shown as thermal ellipsoids at 30% probability level. Hydrogen atoms, perchlorate anions and solvate dichloromethane molecules are omitted for clarity.

**Figure 3.** CV curve for 0.1 mM dichloromethane solution of \([\text{Co}(\text{AcPyOx})_3(\text{ZrPc})](\text{ClO}_4)_2\) 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.
assigned to a redox pair Co$^{3+}$/Co$^{2+}$. The relatively low poten-
tial 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) com-
plexes.\[8\]

Conclusions

One-step synthetic approach allowed to obtain two 
new phthalocyaninate-capped cobalt(III) pseudoclath-
rochelates in moderate yields by direct template con-
densation 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) \(\rightarrow\) 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 voltammeters.

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