

Ditopic Macropolycyclic Complexes: Synthesis of Hybrid Phthalocyaninoclathrochelates

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A remetalation (a capping group exchange) reaction of the boron–antimony-capped iron(II) clathrochelates with zirconium and hafnium(IV) phthalocyanines in CH₂Cl₂/CH₃OH medium afforded the hybrid phthalocyaninoclathrochelates in a practically quantitative yield. The complexes obtained have been characterized both on the basis of elemental analysis, PD mass spectrometry, IR, UV–vis, ⁵⁷Fe Mössbauer, and NMR spectroscopies, and crystallographically. An encapsulated iron(II) ion in an intermediate between a trigonal-prismatic and a trigonal-antiprismatic environment of six nitrogen atoms of the macrobicyclic ligand was found to be in a low-spin state. The cyclic voltammograms show irreversible oxidation and reduction waves assignable to Fe³⁺/Fe²⁺ couples of macrobicyclic fragments and to phthalocyanine macrocycles.

Polytopic transition metal complexes have proved to be promising precursors in creating molecular machines,^{1–4} and electronic and photoelectronic devices^{5,6} using intramolecular and supramolecular electron and energy transfer processes (including those for photoexcited states). Cage complexes with an encapsulated metal ion have been thoroughly studied as luminescent materials, electron carriers in biochemical systems, and sensitizers in photochemical processes (in particular, hydrogen production from water).⁷ Phthalocyanines (Pc) and their complexes with metal ions are exten-

sively employed in creating new photochromic and electrochromic materials.⁸ Ditopic complexes with fragments from these two types of modern coordination compounds are undoubtedly interesting for the design of a new generation of the above-mentioned devices. However, the use of clathrochelates as building blocks is limited by specific conditions of their template synthesis on a d-metal ion matrix by cross-linking of three α -dioximate fragments with Lewis acids that form apical capping groups. These reactions have efficiently been realized only with boron-, tin-, and germanium-containing capping agents and template Fe²⁺, Co²⁺, Co³⁺, and Ru²⁺ ions.⁷ The direct template synthesis has not allowed one to isolate intermediate lacunar (semiclathrochelate) complexes, which are needed to implement a stepwise synthesis of clathrochelates with nonequivalent capping fragments.⁹ We previously proposed a pathway for a stepwise “assembling” of clathrochelates with nonequivalent caps on the element oxide matrix surface.⁹ In many cases, however, its realization is hindered or is hardly possible at all. Antimony(V) triorganyls as efficient capping agents^{10,11} provide a new opportunity for the design and synthesis of compounds of the targeted composition and symmetry. The clathrochelates with triorganylantimony capping groups (Scheme 1), unlike the complexes with other capping fragments, are labile in stepwise exchange (remetalation) reactions involving the capping groups. This makes it possible to use them as precursors in “nontemplate” synthesis of macropolycyclic systems.¹¹

The pathway proposed allows one to obtain complexes with unusual tripodal capping fragments. In particular, we used the Lewis acidity of the metallophthalocyanines for the synthesis of hybrid clathrochelates with phthalocyanine-

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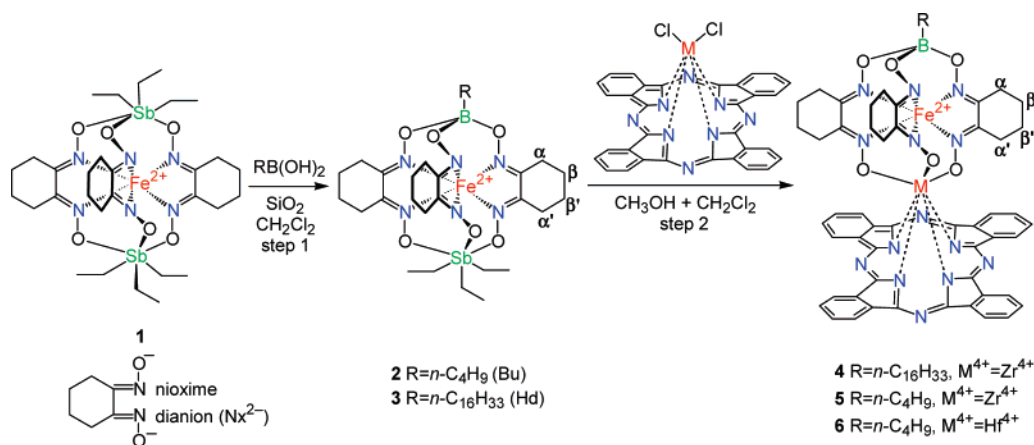
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Scheme 1



containing capping group (Scheme 1). Initially synthesized boron–antimony-capped precursors **2** and **3** in a methylene dichloride–methanol (2:1) medium underwent a remetalation (a capping group exchange) at room temperature with equimolar amounts of $PcHfCl_2$ and $PcZrCl_2$. The fine crystalline products **4–6** were isolated in a practically quantitative yield.

Figure 1 shows the X-ray structure for a hybrid $6 \cdot 3C_6H_6$ phthalocyaninoclathrochelate.¹² The Fe–N distance in this molecule (~ 1.91 Å) is typical for macrobicyclic iron(II) trisdioximates.^{7,13} The geometry of a coordination N_6 -polyhedron (distortion angle $\varphi = 30^\circ$) is intermediate between a trigonal prism (TP, $\varphi = 0^\circ$) and a trigonal antiprism (TAP, $\varphi = 60^\circ$) because of nonequivalence of two capping fragments of the clathrochelate framework. The previously studied boron-containing clathrochelates possess a TP geometry^{13a–c} because a tetrahedral capping B^{3+} ion has a small ionic (Shannon) radius ($r_i = 0.25$ Å), whereas the geometry of the complexes with octahedral cross-linking fragments and greater Shannon radii of the capping ions (Sn^{4+} , $r_i = 0.83$ Å; Ge^{4+} , $r_i = 0.67$ Å; and Sb^{5+} , $r_i = 0.74$ Å) approaches a TAP.^{7,13d} N_4O_3 -Heptacoordinate Hf^{4+} ion ($r_i = 0.90$ Å) belongs to the second type of capping ions. As a result, the clathrochelate framework geometry in BHF-capped molecule **6** is an intermediate between a TP and a TAP. As follows from the quadrupole splitting values (0.21 – 0.26 mm·s⁻¹) in the ⁵⁷Fe Mössbauer spectra,¹⁴ a similar geometry of the encapsulated iron(II) ion coordination polyhedron is also

realized for complexes **2–5**. The isomeric shift values (0.31 – 0.33 mm·s⁻¹) in these spectra are typical for the low-spin iron(II) complexes.

An apparent π -stacking between the “base-to-base” oriented neighboring molecules is a characteristic and specific feature of the crystal structure of **6** (Figure 2). The π -systems of two coplanar “overlapping” pyrrol fragments of phthalocyanine macrocycles of these molecules interact at the distance 3.35 Å. The four coordinated nitrogen atoms of these macrocycles are located in one plane, whereas the coordinating hafnium(IV) ion is displaced by 1.105(1) Å from the N_4 -plane. The phthalocyanine macrocycles are not planar: the dihedral angle Δ between its planar fragments with a bend along a $N_9 \cdots N_{13}$ line is 10.3° . An analogous crystal packing and similar structure of the phthalocyanine ligand have been observed earlier for bis(isopropyl-3-oxo-butanato)-hafnium(IV) phthalocyaninate: N_4O_4 -octacoordinating hafnium(IV) ion is displaced by 1.211 Å from the N_4 -plane, and the Δ angle is 19.5° . The distance between the “overlapping” pyrrol fragments is equal to 3.46 Å.¹⁵

The solution UV–vis spectra of hybrid clathrochelates **4–6** contain intense absorption bands of both chromophoric centers of the molecules. The Fe $d \rightarrow$ cage (dioximate) π^* charge transfer bands at ~ 440 nm ($\epsilon \sim 1 \times 10^4$ mol⁻¹ L cm⁻¹) and the Q-bands of a phthalocyanine fragment at ~ 700 nm ($\epsilon \sim 1 \times 10^5$ mol⁻¹ L cm⁻¹) in the visible region do not overlap, whereas in the UV region a superimposition of the

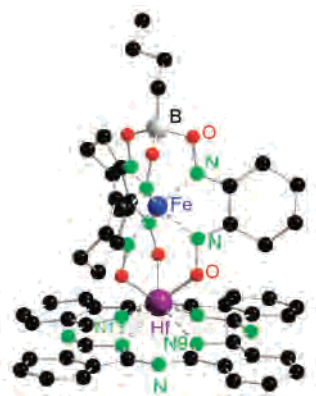


Figure 1. Molecular structure of **6**. H atoms are omitted for clarity.

- (12) Single crystals of complex $6 \cdot 3C_6H_6$ were grown at room temperature from a benzene–isooctane mixture. Crystal data for $6 \cdot 3C_6H_6$ follow: $C_{72}H_{67}BF_6FeHfN_{14}O_6$, $M = 1469.55$, monoclinic, space group $P2_1/c$, $a = 20.568(7)$ Å, $b = 12.213(3)$ Å, $c = 26.971(8)$ Å, $\beta = 108.02(2)^\circ$, $V = 6443(3)$ Å³, $z = 4$, $\rho_{\text{calcd}} = 1.515$ g·cm⁻³, $2\theta_{\text{max}} = 59.7^\circ$, 15481 unique data, $R_1 = 0.0321$, $R_w = 0.0812$, number of parameters 856.
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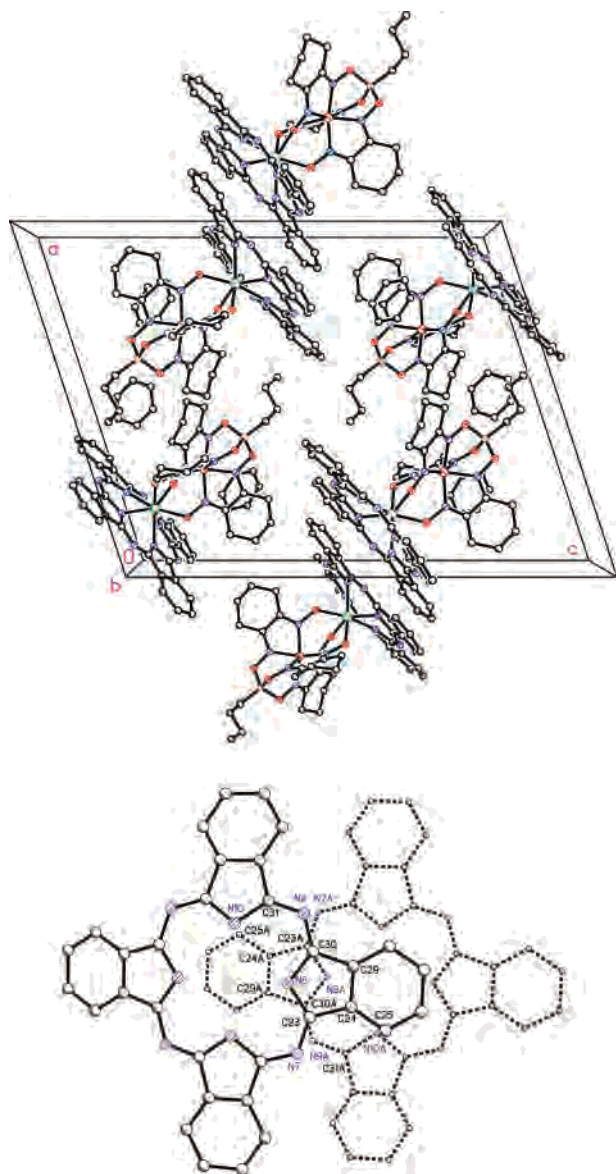


Figure 2. Crystal packing of $6 \cdot 3C_6H_6$ (top) and π -stacking between neighboring phthalocyanine fragments (bottom).

bands assigned to the π - π^* transitions in the cage framework and to the B-band of a phthalocyanine fragment is observed.

The phthalocyanine fragment dramatically affects the shape of the 1H NMR spectra of synthesized clathrochelates: the signals of protons of α - and β -methylene groups of the cyclohexane ring adjacent to this fragment shifted

downfield by ~ 2 ppm because of the magnetic field of the π -electron current in the conjugated macrocyclic system. An analogous effect has been observed previously for the “axial” ligand protons in aluminum, hafnium, and zirconium mono-phthalocyanines.¹⁶ This manifests in the ^{13}C NMR spectra as an essential shift of the signals assigned to α' -C atoms relative to those of α -C atoms: in the case of the synthesized phthalocyaninoclathrochelates $\Delta\delta^{13}C$ caused by a nonequivalence of capping groups is approximately 0.8 ppm, whereas for their BSb-, BSn-, and BGe-capped analogues it does not exceed 0.4 ppm.^{9,11}

The cyclic voltammograms (CVs) for the hybrid compounds demonstrate three oxidation waves (irreversible oxidation at $E_{1/2}^{Ox^2} \approx 1700$ mV, accompanied by destruction of the clathrochelate structure, and quasireversible oxidations localized on the encapsulated iron ion and on the phthalocyanine fragment at $E_{1/2}^{Fe^{2+/3+}} \approx 1300$ mV and $E_{1/2}^{Ox^1} \approx 1000$ mV, respectively) and three reduction processes (quasireversible reductions of the phthalocyanine macrocycle at $E_{1/2}^{Red^1} \approx -650$ mV and $E_{1/2}^{Red^2} \approx -1100$ mV and an irreversible reduction of the clathrochelate framework at $E_{1/2} \approx -1800$ mV with its subsequent destruction), which affect both phthalocyanine and macrobicyclic fragments of the ditopic molecule. A characteristic potential difference of the first oxidation and the first reduction waves of $E_{1/2}^{Ox^1} - E_{1/2}^{Red^1} = 1680 \div 1690$ mV has allowed us to assign them to the phthalocyanine-localized redox processes.⁸ The CV of the initial SbB-capped clathrochelate contains two oxidation waves (a quasireversible wave at $E_{1/2}^{Fe^{2+/3+}} = 950$ mV and an irreversible one at $E_{1/2} = 1900$ mV, caused by the ligand oxidation and accompanied by destruction of the clathrochelate structure) and an irreversible reduction wave at $E_{1/2} = -1800$ mV.

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Supporting Information Available: Elemental analysis, PD-mass, IR, UV-vis, 1H , $^{13}C\{^1H\}$ NMR, ^{57}Fe Mössbauer, electrochemistry, and X-ray crystallography data for the complexes obtained. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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