

# Metal Complexes of 1-Methyltetrabenzooctadehydrocorrin

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**Abstract**—In reaction of 2,3-dihydro-3-[(1-hydroxy-1-methyl-1*H*-isoindol-3-yl)methylene]-1*H*-isoindol-1-one with hydrazine hydrate in the presence of a template agent (metal acetates) in butanol environment metal complexes formed of 1-methyltetrabenzooctadehydrocorrin. A scheme of formation of these compounds was suggested and their spectral characteristics were investigated.

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Corrins are one among interesting groups of porphyrins. The macrocycle of corrin, for example, is contained in the composition of a biologically important compound like vitamin B<sub>12</sub>. The methods of the preparation of corrin derivatives are sufficiently well described in [1–3], however no published data exist on the synthesis and properties of tetrabenzocorrins.

We formerly reported on the use of 2,3-dihydro-3-[(1-oxo-1*H*-isoindol-3-yl)methylene]-1*H*-isoindol-1-one (**I**) in the synthesis of tetrabenzoporphyrins of unsymmetrical structure [4, 5]. Compound **I** can be easily obtained by heating phthalimide (**II**) with zinc acetate at 250–270°C for 30–40 min. Alongside compound **I** as a result of the reaction in keeping with Scheme 1 formed also some 2,3-dihydro-3-[(1-hydroxy-1-methyl-1*H*-isoindol-3-yl)methylene]-1*H*-isoindol-1-one (**III**).

The mixture of compounds **I** and **III** was isolated from the reaction mixture by column chromatography on aluminum oxide. According to GC-MS the fraction of compound **III** in the mixture amounts to 25%. The

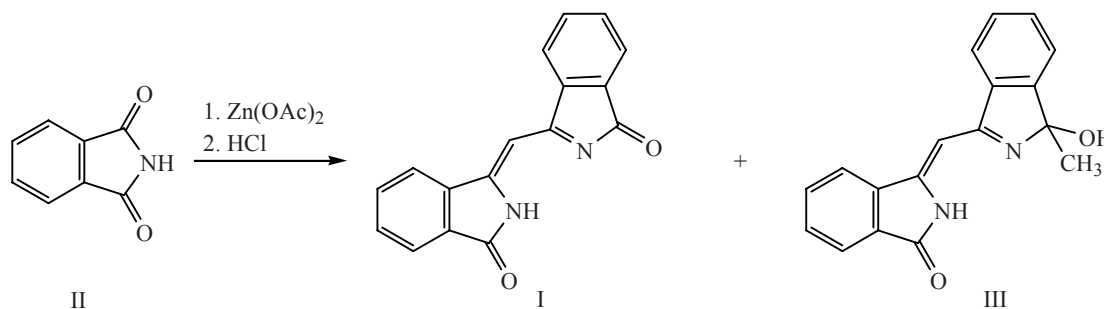
repeated chromatography on silica gel resulted in the separation of compounds **I** and **III**.

Compound **III** is a dark-red powder soluble in polar organic solvents. In the IR spectrum of compound **III** a broad band is observed at 3435 cm<sup>-1</sup> [ $\nu(\text{O}-\text{H}_{\text{associated}})$ ], bands at 3125 and 3020 cm<sup>-1</sup> ( $\nu_{\text{C-H}}$  of benzene rings), a band at 2796 cm<sup>-1</sup> (CH<sub>3</sub>), and a strong band at 1727 cm<sup>-1</sup> [ $\nu(\text{C}=\text{O}_{\text{associated}})$ ].

In the mass spectrum of compound **III** (electron impact ionization) was present the molecular ion peak,  $m/z$  290, and also peaks of its fragment ions,  $m/z$  276, 260, 208.

The electron absorption spectrum of compound **III** registered in acetone (Fig. 1, 1) is characterized by absorption bands with the maxima at 534, 500, 474, and 355 nm. On acidifying with hydrochloric acid the acetone solution changed the color from red to violet, and the absorption bands in visible region suffer a red shift (Fig. 1, 2) by 60–70 nm due to the protonation of the tautomeric form **A** at the nitrogen atom of the isoindolenine moiety providing

**Scheme 1.**



compound **B** with the increased polarization of the molecule as a whole (Scheme 2).

At boiling in 1-butanol of a mixture of compound **III** with hydrazine hydrate in the presence of zinc, copper, or lanthanum acetates as template agents substances formed of a bright green color. After isolation and purification by column chromatography these compounds were characterized as metal complexes of 1-methyltetrabenzooctadecyhydrocorrin **IV–VI**. The formation of complexes **IV–VI** proceeded presumably according to Scheme 3.

Apparently tetramer **VII** formed in the first stage that further reacted with hydrazine hydrate to give hydrazone **VIII**. Compound **VIII** in the presence of a template agent underwent a cyclization and formed metal complexes of 1-methyltetrabenzooctadecyhydrocorrin **IV–VI**.

A fact that calls for attention is the complex formation under relatively mild conditions not only with zinc and copper, but also with lanthanum that possesses a large ionic radius. This suggests that the macrocycle of the 1-methyltetrabenzooctadecyhydrocorrin is less rigid than that of tetrabenzoporphyrin and its derivatives. Even in the case of *meso*-phenyl-substituted tetrabenzoporphyrins possessing a nonplanar macroring their complexing with the metals of large ionic radii occurs under far more stringent conditions, e.g., in boiling DMF [6].

In formation of compound **VI** the acetate extraligand was replaced by a hydroxyl.

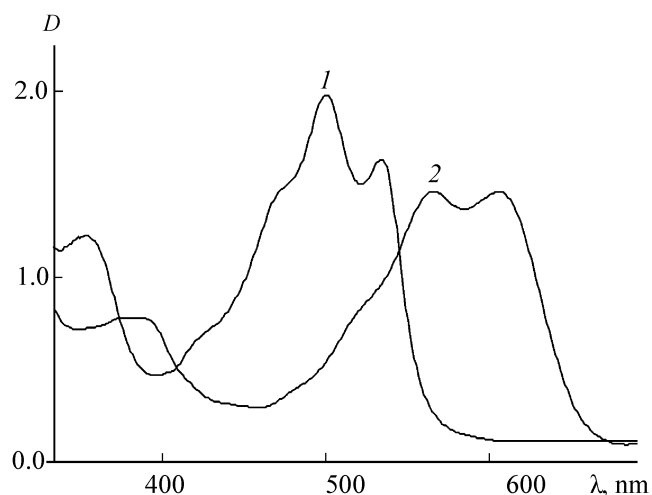
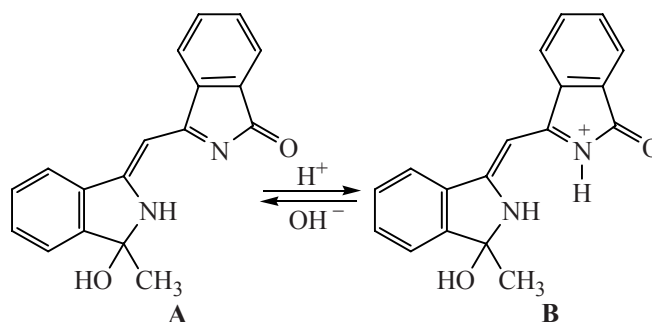
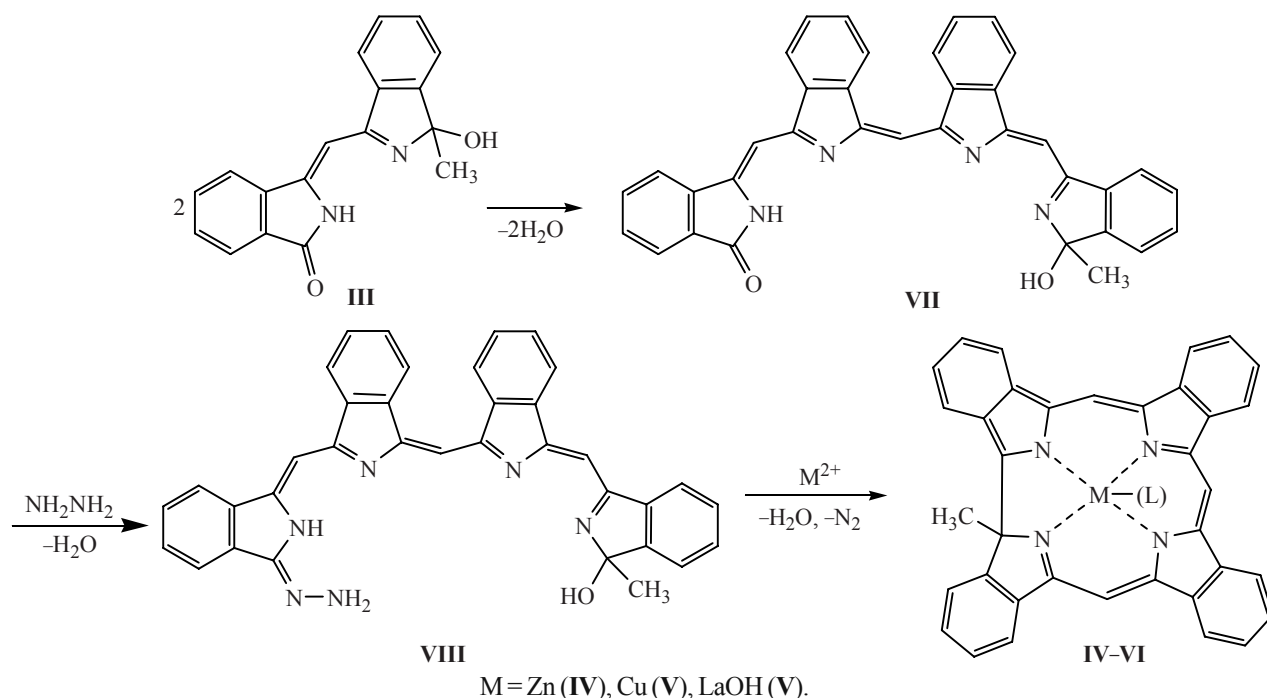


Fig. 1. Electron absorption spectra of compound **III**: (1) in acetone; (2) in acetone acidified with hydrochloric acid.

Scheme 2.



Scheme 3.



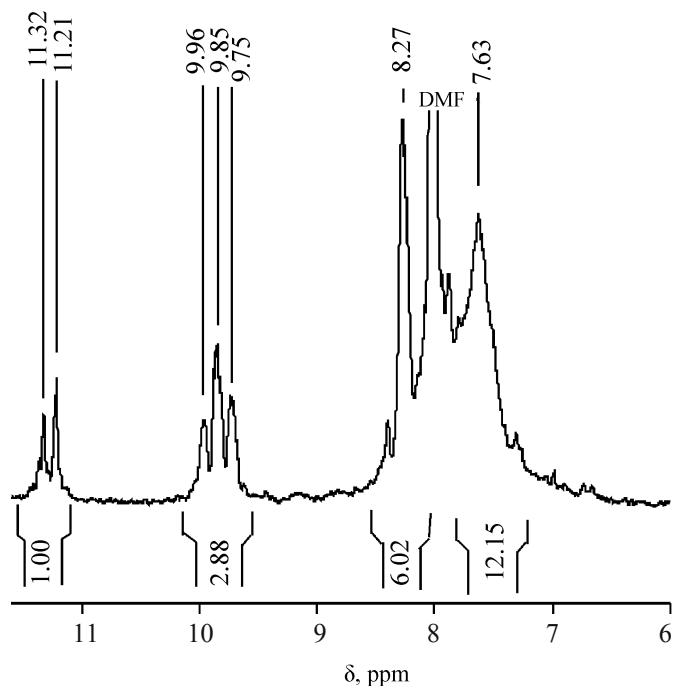


Fig. 2.  $^1\text{H}$  NMR spectrum of compound **IV** in  $\text{DMF-}d_7$ .

Compounds **IV–VI** are dark-green powders well soluble in organic solvents. Their composition and structure were confirmed by elemental analysis, vibration,  $^1\text{H}$  NMR, electronic, and mass spectra.

The IR spectra of compounds **IV–VI** contain a series of common absorption bands. In the region  $2792\text{--}2796\text{ cm}^{-1}$  bands are present indicating the presence of methyl groups, the bands in the region  $1711\text{--}1703$ ,  $1598\text{--}1567$ ,  $1455\text{--}1448$ ,  $1141\text{--}1133$ , and  $830\text{--}816\text{ cm}^{-1}$  belong to the stretching and bending vibrations of C–C and C–N bonds in the macrocycle.

In the  $^1\text{H}$  NMR spectrum of compound **IV** (Fig. 2) registered in  $\text{DMF-}d_7$  the most downfield signal is an unsymmetrical doublet at  $11.32\text{--}11.21$  ppm corresponding to the resonance of one *meso*-proton in the position 5 of the macrocycle. The triplet at  $9.96\text{--}9.75$  ppm characterized the resonance of three protons from the methyl group. The singlet at  $8.27$  ppm corresponded to the resonance of two *meso*-protons in the positions 10 and 15 of the macrocycle and of four protons of the isoindole fragment linked to a methyl group. Finally, the multiplet in the region  $7.90\text{--}7.30$  ppm belongs to the resonance of other 12 protons of the rest three isoindole fragments.

In the mass spectrum (MALDI–TOF) of the copper complex **V** the peak was observed of the deprotonated molecular ion,  $m/z$  572. The isotope composition of the cluster  $[M - 1]^+$  (Fig. 3a) is in its character fairly close to that calculated for compound  $\text{C}_{36}\text{H}_{21}\text{CuN}_4$  (Fig. 3b). The

mass spectrum (ESI) of the lanthanum complex **VI** contained a peak,  $m/z$  663  $[M - 3]^+$ , and also another one,  $m/z$  651, corresponding to the fragment  $[M - 15]^+$  formed by the cleavage of the angular methyl group.

The electron absorption spectra of complexes **IV–VI** (Fig. 4) are very similar. They contain in the visible region the Soret band and the *Q* band split in two components. In the spectra of porphyrins metal complexes belonging to the symmetry point group  $D_{4h}$ , e.g., zinc tetrabenzoporphyrinate, the single *Q* band corresponds to the electron transitions from the HOMO ( $A_{1g}$ ) to two perpendicularly oriented degenerate orbitals  $E_u^*$ . In the spectra of compounds **IV–VI** due to the unsymmetrical form of

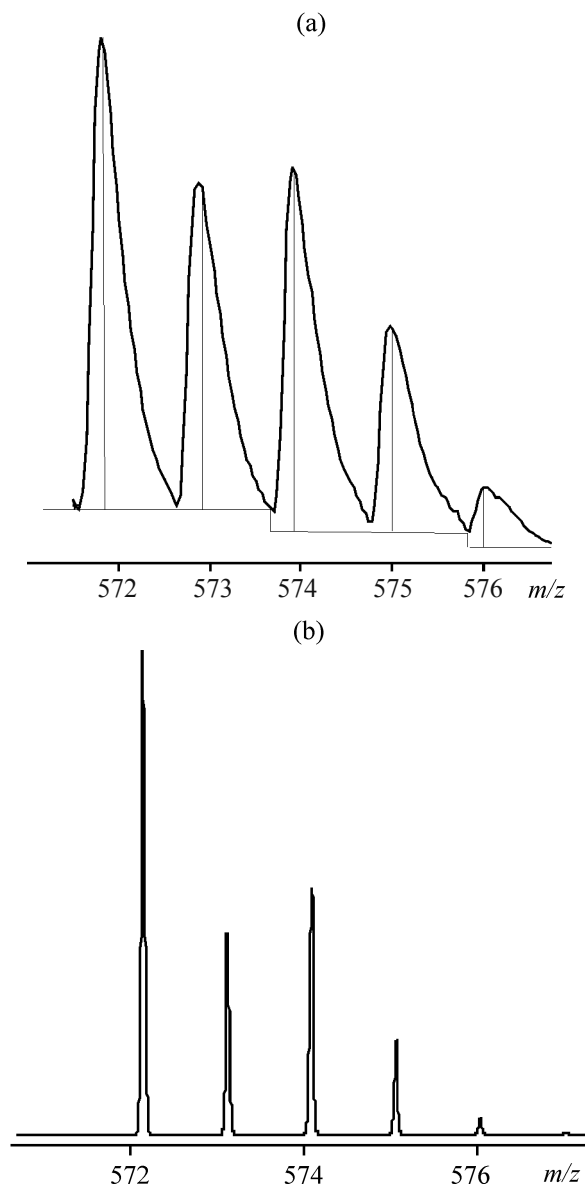
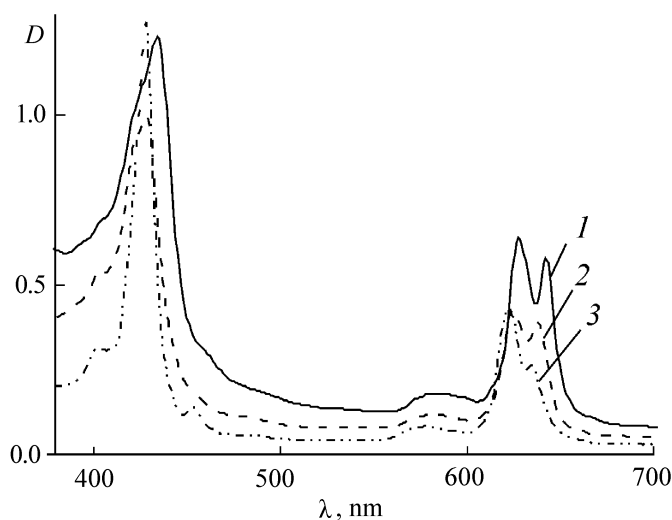


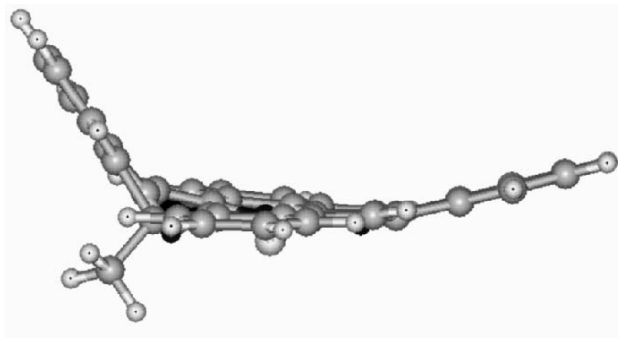
Fig. 3. Isotope composition of the cluster  $[M - 1]^+$  for compound **V**: (a) experimental; (b) calculated.

the macrocycle the degeneration is removed, and the Q band is split in two components. A similar spectral pattern is characteristic also of unsymmetrical porphyrazines [7] and azaporphyrins [8].

As to the position of the bands in the electron absorption spectra of complexes **IV–VI**, the Soret band and the short-wave component of the Q band are situated in the same regions as in the spectra of tetrabenzoporphyrin metal complexes [9, 10]. However the intensity ratio of the absorption bands changed considerably. Whereas in the electronic spectrum of zinc tetrabenzoporphyrinate the intensity ratio of Soret and Q bands was 1:0.34 [11], in the spectrum of zinc complex **IV** (Fig. 4, 1) it is for the long-wave component of the Q band 1:0.47, for the short-wave component, 1:0.52. The enhanced intensity of the Q band evidenced the release of the quasiband from the electron transitions  $A_{1g} > E_u^*$ . In the spectrum of copper complex **V** (Fig. 4, 2) compared to compound **IV** a small blue shift is observed of the absorption bands due to the increase in the strength of the metal–ligand bond. In the spectrum of lanthanum complex **VI** (Fig. 4, 3) the observed blue shift of the main absorption bands is still larger, but here its reason apparently lies in the effect of the ionic radius of the metal on the geometric structure of the macrocycle. A similar pattern was formerly observed on the complexes of *meso*-tetraphenyltetrabenzoporphyrin with three- and four-valent metals [12]. However in the spectrum of complex **VI** the blue shift of the absorption bands as compared to the spectrum of zinc complex **IV** is just 5–6 nm indicating that complex **IV** is non-planar,



**Fig. 4.** Electron absorption spectra in toluene. (1) compound **IV**, (2) compound **V**, (3) compound **VI**.



**Fig. 5.** Spatial arrangement of compound **IV** according to calculations by method AM1.

and further distortion of the macrocycle in compound **VI** does not lead to essential changes in the spectral characteristics of the latter. To confirm this assumption we performed the quantum-chemical calculation of the molecule **IV** using semiempirical method AM1. The spatial structure obtained by the calculations is presented in Fig. 5. As seen the molecule of complex **IV** actually is non-planar; therewith three isoindole fragments are situated in one plane, but the fourth fragment, linked to a methyl group, is deviated from this plane by an angle over  $70^\circ$ . Thus the results of the quantum-chemical calculations are in good agreement with the spectral characteristics of compounds obtained.

## EXPERIMENTAL

Electron absorption spectra of compounds obtained were measured on a spectrophotometer Hitachi UV-2001.  $^1\text{H}$  NMR spectrum in  $\text{DMF-}d_7$  was registered on a spectrometer Bruker WM-250 (250 MHz, internal reference TMS). IR spectra were recorded on a spectrophotometer Avatar 360 FT-IR in the region  $400\text{--}4000\text{ cm}^{-1}$  from the films on a glass TII. GC-MS measurements were carried out on an instrument Varian Saturn 2000R. Mass spectrum MALDI-TOF was taken on an instrument Bruker Reflex III (dithranol matrix), mass spectrum ESI, on a Perkin-Elmer SCIEX API 100 instrument. Elemental analyses were performed on a FlashEA 1112 CHNS-O Analyzer.

**2,3-Dihydro-3-[(1-hydroxy-1-methyl-1*H*-isoindol-3-yl)methylene]-1*H*-isoindol-1-one (III).** A mixture of 16 g (0.11 mol) of phthalimide and 25 g (0.11 mol) of zinc acetate dihydrate was heated at  $230^\circ\text{C}$  for 30 min, the reaction mixture was cooled, dispersed, boiled for 10 min in 100 ml of 10% sodium hydroxide solution, filtered off, and washed with 50 ml of water. The precipitate was boiled for 10 min in 100 ml of 10%

hydrochloric acid, it was filtered off and washed with water till pH 7. The residue was dissolved in acetone and subjected to chromatography on a column packed with aluminum oxide of II grade of activity. The red zone was collected (eluent acetone). On removing the solvent the residue was subjected to chromatography on silica gel 60 (elution with a mixture toluene–acetone, 2:1, v/v), collecting the first red zone. Yield 1.2 g (8%), red powder, soluble in acetone, pyridine, DMF. Electron absorption spectrum,  $\lambda_{\max}$ , nm ( $D/D_{\max}$ ), (acetone): 534 (0.83), 500 (1.00), 474 (0.75), 355 (0.62); (acetone + HCl): 606 (1.00), 565 (1.00), 381 (0.53). IR spectrum,  $\nu$ ,  $\text{C}\mu^{-1}$ : 3435, 3125, 3020, 2796, 1727, 1406. Mass spectrum (Electron impact, 80 eV),  $m/z$  ( $I_{\text{rel}}$ , %): 290  $[M]^+$  (10), 276  $[M - \text{CH}_3]^+$  (17), 260  $[M - \text{CH}_3\text{OH}]$  (11), 208  $[M - \text{HCONH}_2 - \text{CH}_3\text{OH} - 5]^+$  (100). Found, %: C 74.39; H 4.91; N 9.22.  $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_2$ . Calculated, %: C 74.47; H 4.86; N 9.65.

**Complexes of 1-methyltetrabenzooctadecydrocortin with zinc (IV), copper (V), and lanthanum (VI).** In 10 ml of 1-butanol was dissolved 0.25 g (8.6 mmol) of compound III, 1 ml of 70% hydrazine hydrate and 0.3 g of acetate of an appropriate metal were added, and the mixture was heated at reflux for 3 h. On cooling 10 ml of hexane was added, and the separated precipitate was filtered off. The filtrate was subjected to chromatography on a column packed with aluminum oxide of II grade of activity (eluent toluene), collecting the first bright-green zone.

**Zinc 1-methyltetrabenzooctadecydrocortinate (IV).** Yield 60 mg (25%), dark-green powder. Electron absorption spectrum (toluene),  $\lambda_{\max}$  ( $\log \epsilon$ ): 642 (3.93), 627 (4.19), 434 (4.60). IR spectrum,  $\text{cm}^{-1}$ : 2792, 1711, 1577, 1450, 1141, 816.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 11.32–11.21 d (1H), 9.96–9.75 t (3H), 8.27 s (6H), 7.90–7.30 m (12H). Found, %: C 75.33; H 3.98; N 9.05.  $\text{C}_{36}\text{H}_{22}\text{N}_4\text{Zn}$ . Calculated, %: C 75.07; H 3.85; N 9.73.

**Copper 1-methyltetrabenzooctadecydrocortinate (V).** Yield 53 mg (22%), dark-green powder.

Electron absorption spectrum (toluene),  $\lambda_{\max}$  ( $\log \epsilon$ ): 638 (3.89), 624 (4.07), 428 (4.57). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2793, 1709, 1598, 1448, 1136, 830. Mass spectrum (MALDI–TOF):  $m/z$  572  $[M - 1]^+$  ( $I_{\text{rel}}$  100%). Found, %: C 75.74; H 4.02; N 9.22.  $\text{C}_{36}\text{H}_{22}\text{CuN}_4$ . Calculated, %: C 75.31; H 3.86; N 9.76.

**Hydroxylanthanum 1-methyltetrabenzooctadecydrocortinate (VI).** Yield 48 mg (17%), dark-green powder. Electron absorption spectrum (toluene),  $\lambda_{\max}$  ( $\log \epsilon$ ): 634 (3.81), 622 (4.05), 428 (4.58). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2796, 1703, 1567, 1455, 1133, 821. Mass spectrum (ESI),  $m/z$  ( $I_{\text{rel}}$ , %): 663  $[M - 3]^+$  (100), 651  $[M - 15]^+$  (30). Found, %: C 65.02; H 3.76; N 7.95.  $\text{C}_{36}\text{H}_{23}\text{LaN}_4\text{O}$ . Calculated, %: C 64.87; H 3.48; N 8.41.

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