

## Synthesis and Properties of Hexa(4-*tert*-butylphenoxy) Substituted Trithiadodecaaza[30]hexaphyrin and Its Metal Complexes

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Dedicated to Professor Oscar I. Koifman on the occasion of his 70th birthday

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*A new hexa(4-*tert*-butylphenoxy) substituted trithiadodecaaza[30]hexaphyrin was obtained by reaction of 4,5-bis(4-*tert*-butylphenoxy)phthalonitrile and 2,5-diamino-1,3,4-thiadiazole in ethylene glycol, as well as its Ni<sup>II</sup>, Cu<sup>II</sup>, Co<sup>II</sup>, Zn<sup>II</sup> 3:1 metallocomplexes were synthesized. All the compounds were characterized by UV-Vis, IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy, mass spectrometry and elemental analysis.*

**Keywords:** Synthesis, thiadiazole, expanded porphyrinoids, metal complexes.

## Синтез и свойства гекса(4-*трет*-бутилфеноксид)замещенного Тритиадодэкааза[30]гексафрина и его металлокомплексов

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Посвящается Член-корреспонденту РАН Оскару Иосифовичу Койфману по случаю его 70-летнего юбилея

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*Взаимодействием 4,5-бис(4-*трет*-бутилфеноксид)фталонитрила с 2,5-диамино-1,3,4-тиадиазолом в этиленгликоле получен новый гекса(4-*трет*-бутилфеноксид)замещенный тритиадодэкааза[30]гексафрин, а так же его металлокомплексы состава 3:1 с Ni<sup>II</sup>, Cu<sup>II</sup>, Co<sup>II</sup> и Zn<sup>II</sup>.*

**Ключевые слова:** Синтез, тиадиазол, порфириноиды с увеличенной координационной полостью, металлокомплексы.

## Introduction

Trithiadiazoleporphyrinoids are known as aza-analogues of expanded porphyrinoids that consist of three alternating thiadiazole units and three isoindole moieties connected to each other via aza-bridges.<sup>[1,2]</sup> These compounds possess a variety of unprecedented properties such as non-aromatic character despite formally fitting the Hückel's rule,<sup>[3,4]</sup> tautomeric behavior,<sup>[5,6]</sup> high thermal stability,<sup>[7]</sup> and ability to accommodate up to three transition metals such as Ni<sup>2+</sup>, Cu<sup>2+</sup> or Co<sup>2+</sup> within their enlarged coordination cavities.<sup>[1,2]</sup> Moreover, presence of three thiadiazole subunits makes these compounds promising candidates for a wide area of applications, similar to other thiadiazole-containing polymers and small molecules that find their use in medicinal, agricultural<sup>[8]</sup> and photovoltaic sectors.<sup>[9,10]</sup>

With the goal of detailed characterization and revealing potential applications of this young class of compounds, substituted and unsubstituted thiadiazoloporphyrinoids have been obtained very recently.<sup>[3,7,11,12]</sup> It has been found that unsubstituted thiadiazoloporphyrinoids are insoluble in most of organic solvents. An introduction of bulky substituents on the periphery of their molecules led to a significant increase of their solubility that allowed a purification and characterization. Herein, in the present communication, we report a synthesis of a macroheterocyclic compound bearing six 4-*tert*-butylphenoxy groups that has been synthesized for the first time and fully characterized.

## Experimental

MALDI TOF MS spectra (Bruker Reflex III spectrometer), NMR spectra (Bruker AC-300 instrument) were carried out within collaboration of IRLON (ISUCT) and Universidad Autonoma de Madrid. Chemical shifts ( $\delta$ ) are expressed in parts per million (ppm) relative to tetramethylsilane. The coupling constants ( $J$ ) are given in hertz (Hz). UV-vis spectra were recorded with a Jasco V-660 spectrophotometer using CHCl<sub>3</sub> as the solvent (1 cm path length quartz cell). Elemental analysis was performed on Flach EA 1112 instrument. IR spectra were recorded on Avatar 360 FT-IR ESP spectrophotometer. Column chromatography was carried out on silica gel (Fluka, 40-200 mesh). Analytical TLC was carried out on pre-coated sheets with silica gel (0.2 mm thick, Merck).

4,5-Bis(4-*tert*-butylphenoxy)phthalonitrile (**2**)<sup>[13]</sup> and 2,5-diamino-1,3,4-thiadiazole (**3**)<sup>[14]</sup> were prepared according to the known procedures. All the other solvents and reagents were used without further purification.

*Synthesis of 2,3,14,15,26,27-hexa[4-*tert*-butylphenoxy]-5,36:12,17:24,29-triimino-7,10:19,22:31,34-trithio-[f,p,z]-tribenzo-1,2,4,9,11,12,14,19,21,22,24,29-dodecazacyclotriaconta-2,4,6,8,10,12,14,16,18,20,22, 24,26,28,30-pentadecaene, 1.* 0.25 g (0.58 mmol) of 4,5-bis(4-*tert*-butylphenoxy)phthalonitrile **2** was heated in 10 mL of anhydrous ethylene glycol at 80°C, following by addition of 0.068 g (0.58 mmol) of 2,5-diamino-1,3,4-thiadiazole **3**. After the temperature of the reaction was slowly raised to reflux, stirring was continued for the next 36 h, following the completion of the reaction by TLC. After the reaction mixture was cooled to r.t., it was diluted with 100 mL of water resulting in a formation of a precipitate that was filtered, washed with water, methanol and hexane, and further extracted with chloroform. Final purification was performed by column chromatography using silica gel as solid phase and chloroform as mobile phase. The solvent was rotary evaporated affording orange crystalline solid that was dried

under vacuum for 2 hours at 60°C. Yield: 30%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS)  $\delta$  ppm: 12.03 (s., 3H, NH), 7.35 (s., 6H, -CH=), 7.32-7.25 (d,  $J$  = 9 Hz, 12H, -CH=), 7.10-7.02 (d,  $J$  = 9 Hz, 12H, -CH=), 1.26 (s., 18H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz)  $\delta$  ppm: 31, 34, 119, 127, 147, 152, 153, 170. IR (KBr)  $\nu$  cm<sup>-1</sup>: 3431, 3230, 2963, 2869, 1625, 1506, 1479, 1456, 1369, 1274, 1219, 1175, 993, 881, 722. UV-Vis (CHCl<sub>3</sub>)  $\lambda_{\text{max}}$  nm (lg $\epsilon$ , dm<sup>3</sup>·mol<sup>-1</sup>·cm<sup>-1</sup>): 293 (4.72), 400(4.94), 421 (4.97), 470 (4.32), 508 (4.15). MS (MALDI TOF, dithranol)  $m/z$ : 1570.6 [M+H]<sup>+</sup>, 1592.5 [M+Na]<sup>+</sup>. Calc. for C<sub>90</sub>H<sub>88</sub>N<sub>15</sub>O<sub>6</sub>S<sub>3</sub><sup>+</sup>: EM=1570.6 [M+H]<sup>+</sup>; C<sub>90</sub>H<sub>87</sub>N<sub>15</sub>NaO<sub>6</sub>S<sub>3</sub><sup>+</sup>: EM = 1592.6 [M+Na]<sup>+</sup>. Found, %: C 67.2, H 5.7, N 12.8, S 5.5; Calc. for C<sub>90</sub>H<sub>87</sub>N<sub>15</sub>O<sub>6</sub>S<sub>3</sub><sup>+</sup>, %: C 68.8, H 5.5, N 13.3, S 6.1

*Synthesis of Ni(II) Ia, Co(II) Ib, Cu(II) Ic and Zn(II) Id complexes of 2,3,14,15,26,27-hexa[4-*tert*-butylphenoxy]-5,36:12,17:24,29-triimino-7,10:19,22:31,34-trithio-[f,p,z]-tribenzo-1,2,4,9,11,12,14,19,21,22,24,29-dodecazacyclotriaconta-2,4,6,8,10,12,14,16,18,20,22,24,26,28,30-pentadecaene.* General procedure: a mixture of 0.05 g (0.032 mmol) of **1** (0.159 mmol) of the corresponding metal chloride and 4.9  $\mu$ L (0.032 mmol) of 1,8-diazabicycloundec-7-ene (DBU) in 5 mL of DMF was heated for 5 hours at 120°C. After cooling of the reaction mass to room temperature, 25 mL of water were added and the resulting precipitate was filtered, washed with water, hot methanol and the corresponding complex compound was extracted with chloroform. The solvent was rotary evaporated and the product was dried under vacuum for 2 hours at 60°C to yield red-brown powders.

**Ia** was obtained using 0.021 g of anhydrous NiCl<sub>2</sub>. Yield 80%. IR (KBr)  $\nu$  cm<sup>-1</sup>: 3430, 2958, 2869, 1604, 1537, 1506, 1473, 1442, 1384, 1269, 1215, 1114, 1054, 912, 839, 738. UV-Vis (CHCl<sub>3</sub>)  $\lambda_{\text{max}}$  nm (lg $\epsilon$ , dm<sup>3</sup>·mol<sup>-1</sup>·cm<sup>-1</sup>): 280 (4.77), 450 (4.31). MS (MALDI-TOF, dithranol)  $m/z$ : 1756.4 [C<sub>90</sub>H<sub>84</sub>Ni<sub>3</sub>N<sub>15</sub>O<sub>7</sub>S<sub>3</sub>]<sup>+</sup>. Calc. for C<sub>90</sub>H<sub>84</sub>Ni<sub>3</sub>N<sub>15</sub>O<sub>7</sub>S<sub>3</sub><sup>+</sup>: EM=1756.4 [Mc+3Ni+O]<sup>+</sup>.

**Ib** was obtained using 0.038 g of CoCl<sub>2</sub>·6H<sub>2</sub>O. Yield 92%. IR (KBr)  $\nu$  cm<sup>-1</sup>: 3448, 2959, 2863, 1603, 1572, 1474, 1436, 1387, 1264, 1214, 1140, 1047, 906, 883, 737. UV-Vis (CHCl<sub>3</sub>)  $\lambda_{\text{max}}$  nm (lg $\epsilon$ , dm<sup>3</sup>·mol<sup>-1</sup>·cm<sup>-1</sup>): 290 (4.70), 415 (4.37). MS (MALDI-TOF, dithranol)  $m/z$ : 1759.4 [C<sub>90</sub>H<sub>84</sub>Co<sub>3</sub>N<sub>15</sub>O<sub>7</sub>S<sub>3</sub>]<sup>+</sup>. Calc. for C<sub>90</sub>H<sub>84</sub>Co<sub>3</sub>N<sub>15</sub>O<sub>7</sub>S<sub>3</sub><sup>+</sup>: EM=1759.4 [Mc+3Co+O]<sup>+</sup>.

**Ic** was obtained using 0.021 g of anhydrous CuCl<sub>2</sub>. Yield 79%. IR (KBr)  $\nu$  cm<sup>-1</sup>: 3421, 2958, 2923, 2864, 1599, 1509, 1471, 1437, 1373, 1266, 1217, 1109, 1037, 893, 834, 743. UV-Vis (CHCl<sub>3</sub>)  $\lambda_{\text{max}}$  nm (lg $\epsilon$ , dm<sup>3</sup>·mol<sup>-1</sup>·cm<sup>-1</sup>): 268 (4.64), 410 (4.36). MS (MALDI TOF, dithranol)  $m/z$ : 1771.2 [C<sub>90</sub>H<sub>84</sub>Cu<sub>3</sub>N<sub>15</sub>O<sub>7</sub>S<sub>3</sub>]<sup>+</sup>. Calc. for C<sub>90</sub>H<sub>84</sub>Cu<sub>3</sub>N<sub>15</sub>O<sub>7</sub>S<sub>3</sub><sup>+</sup>: EM=1771.4 [Mc+3Cu+O]<sup>+</sup>.

**Id** was obtained using 0.022 g of anhydrous ZnCl<sub>2</sub>. Yield 67%. IR (KBr)  $\nu$  cm<sup>-1</sup>: 3433, 2958, 2926, 2866, 1598, 1508, 1472, 1434, 1369, 1269, 1235, 1137, 1027, 882, 831, 742. UV-Vis (CHCl<sub>3</sub>)  $\lambda_{\text{max}}$  nm (lg $\epsilon$ , dm<sup>3</sup>·mol<sup>-1</sup>·cm<sup>-1</sup>): 292 (4.58), 425 (4.66). MS (MALDI-TOF, dithranol)  $m/z$ : 1774.2 [C<sub>90</sub>H<sub>84</sub>Zn<sub>3</sub>N<sub>15</sub>O<sub>7</sub>S<sub>3</sub>]<sup>+</sup>. Calc. for C<sub>90</sub>H<sub>84</sub>Zn<sub>3</sub>N<sub>15</sub>O<sub>7</sub>S<sub>3</sub><sup>+</sup>: EM=1774.4 [Mc+3Zn+O]<sup>+</sup>.

## Results and Discussion

As it has been shown in previous works, functional derivatives of phthalonitriles such as diimino- or alkoxyiminoisoindolines were successfully used as precursors to obtain thiadiazoloporphyrinoids. However, in some cases it was also possible to obtain a hemiporphyrine directly from an appropriately chosen dinitrile precursor. So metal free compound **1** was obtained by the condensation of 4,5-bis(4-*tert*-butylphenoxy)phthalonitrile **2** and 2,5-diamino-1,3,4-thiadiazole **3** in ethylene glycol<sup>[15,16]</sup> following Scheme 1. A higher temperature of synthesis was enough to terminate crossover cyclization of macrosystem of ABABAB-type.

High solubility in organic solvents of **1** allows its purification by column chromatography on silica gel, eluting the desirable product as the first fraction by use of chloroform. Macroheterocyclic compound **1** was characterized by mass-spectrometry,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, UV-Vis, IR-spectroscopy and elemental analysis. An intensive signal at  $1570.6\text{ m/z}$  that corresponds to molecular ion  $[\text{M}+\text{H}]^+$  was detected in mass-spectrum of **1** along with a signal of lower intensity at  $1592.5\text{ m/z}$ , corresponding to  $[\text{M}+\text{Na}]^+$  ion.

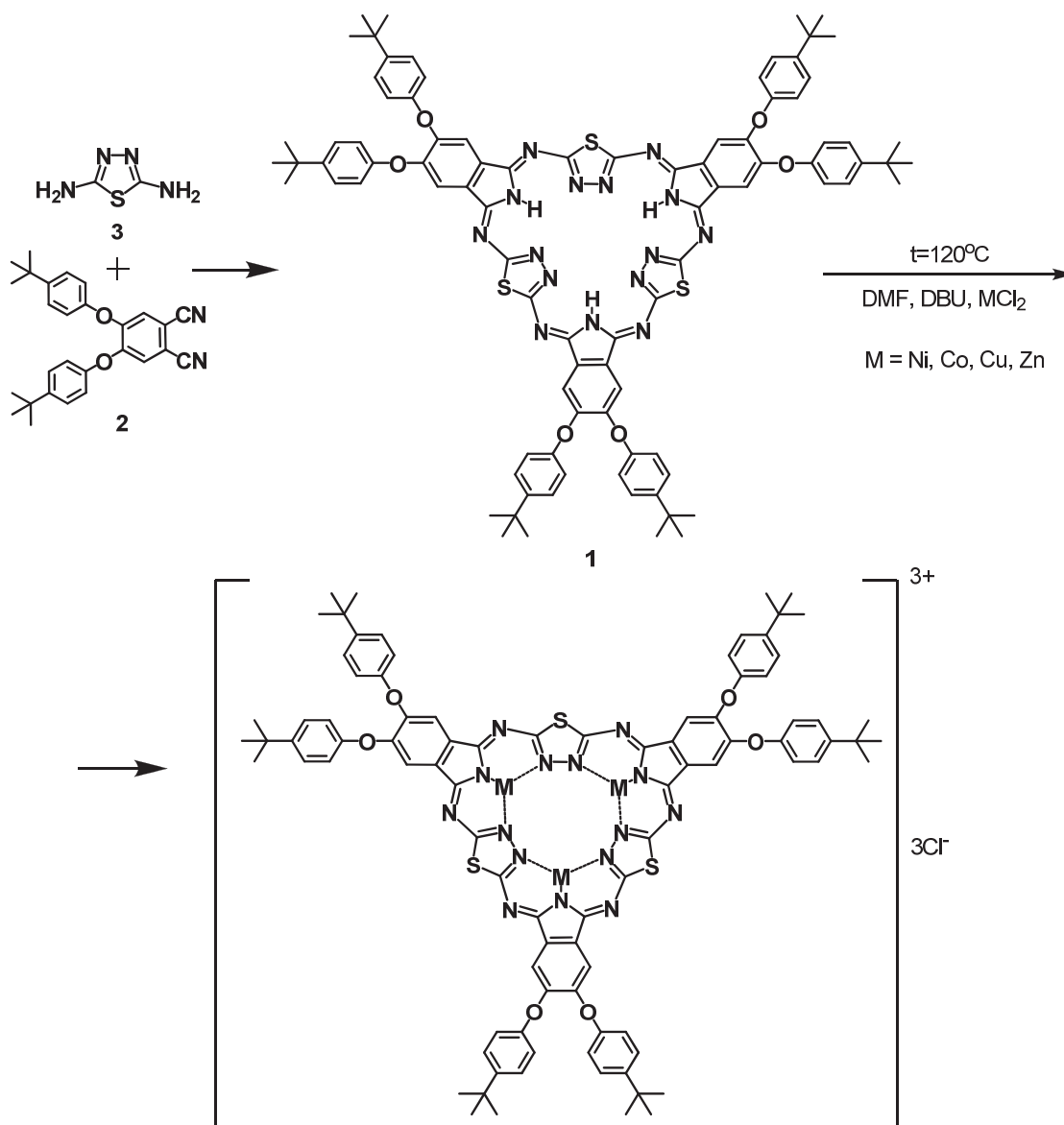
In the  $^1\text{H}$  NMR spectrum of **1** in  $\text{CDCl}_3$  (Figure 1), a singlet at 1.26 (a) ppm induced by protons resonance of methyl groups of 4-*tert*-butyl fragments was revealed. Two doublets at 7.32, 7.29 and 7.05, 7.02 ppm values can be assigned to the phenylene protons resonance of *p-tert*-butylphenoxy groups, the constants of spin-spin interaction are equal to 9 Hz. Singlet at 12 ppm (d) is induced by resonance of protons of the inner NH-groups. This proves that all the three protons are equivalent in a symmetric macrocyclic core. Appearance of this signal in a low field confirms a nonaromatic character of macrocyclic system of **1**.

The  $^{13}\text{C}$  NMR spectrum of **1** as well as assignment of the signals are shown in the Figure 2.

The bands at  $2963$  and  $2869\text{ cm}^{-1}$  detected in the infrared-spectrum of **1** can be correlated to symmetric and asymmetric vibrations of C-H bonds of methyl groups of 4-*tert*-butyl fragments. It should be noted that in the spectrum of metal-free compound **1**, a signal corresponding to vibrations of inner N-H bond at  $3230\text{ cm}^{-1}$  is observed.

In UV-Vis spectrum of **1** (Figure 3), the shape of the spectral curve together with a strong absorption maxima located in the UV and visible regions ( $400$  and  $421\text{ nm}$ ) are typical for macrocyclic compounds of ABABAB-type.<sup>[1-3]</sup> Additionally, the location of the absorption maxima in the violet part of visible spectrum confirms a non-aromatic character of **1**.

Metal complexes **1a-d** were obtained by metallation of **1** with corresponding metal chlorides (Cu, Co, Ni, Zn) in DMF at  $120^\circ\text{C}$  for 5 hours in presence of a drop of DBU (Scheme 1). Reaction was controlled by TLC and UV-Vis spectroscopy. The compounds **1a-d** were purified by washing



Scheme 1.

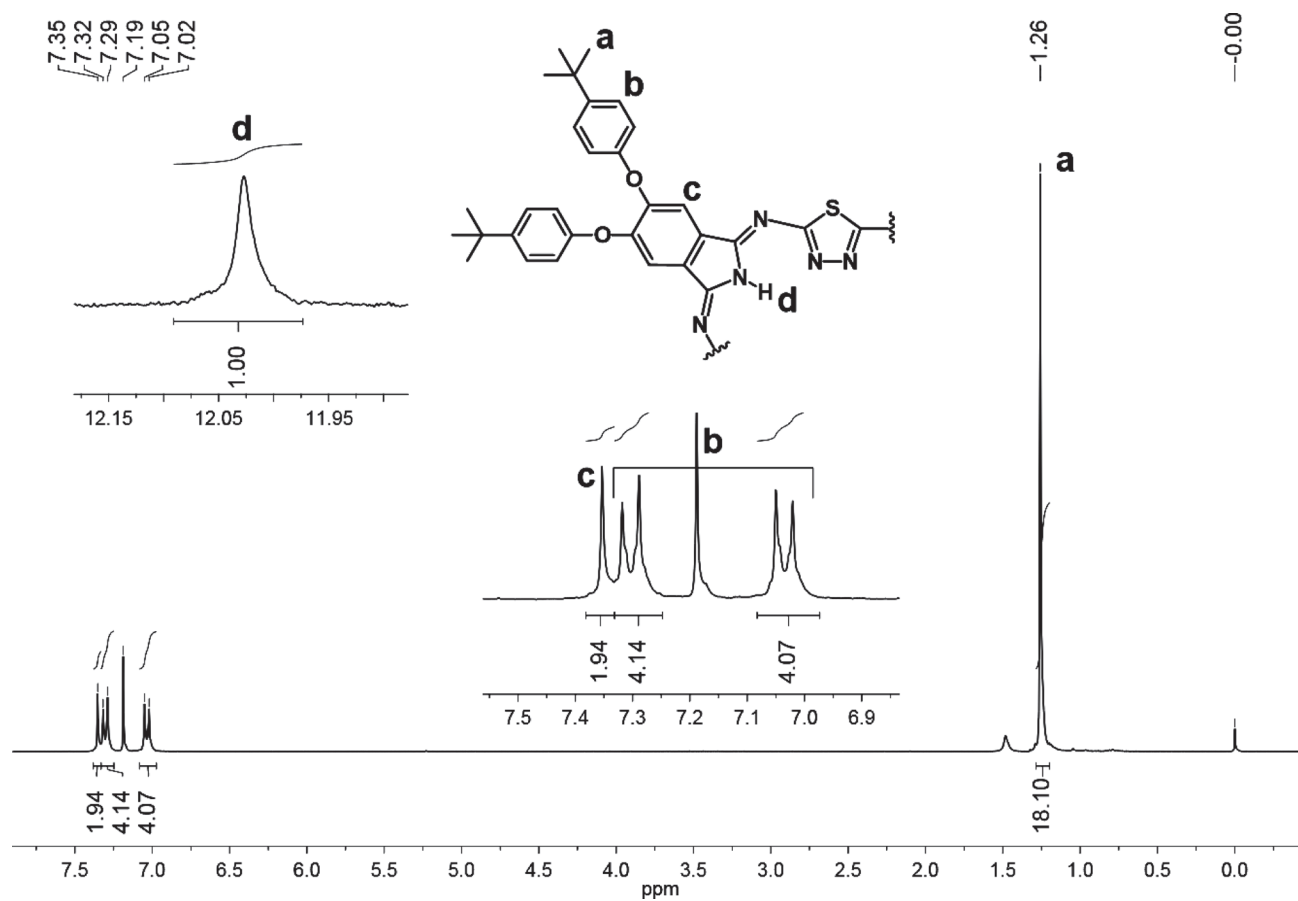


Figure 1. <sup>1</sup>H NMR spectrum for **3** in CDCl<sub>3</sub>.

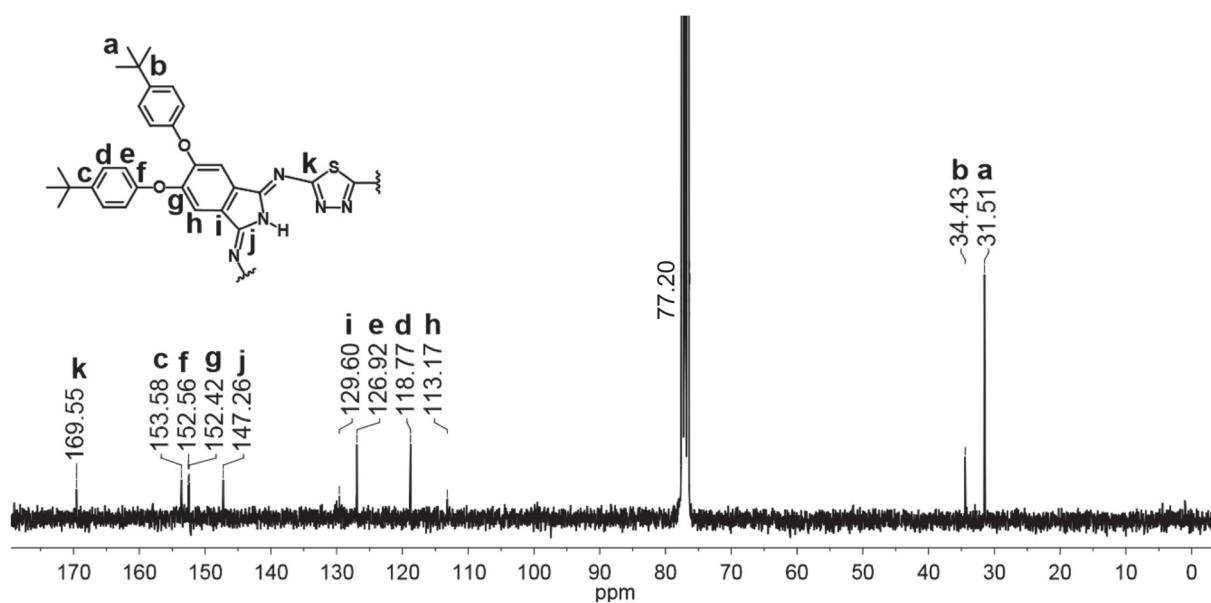
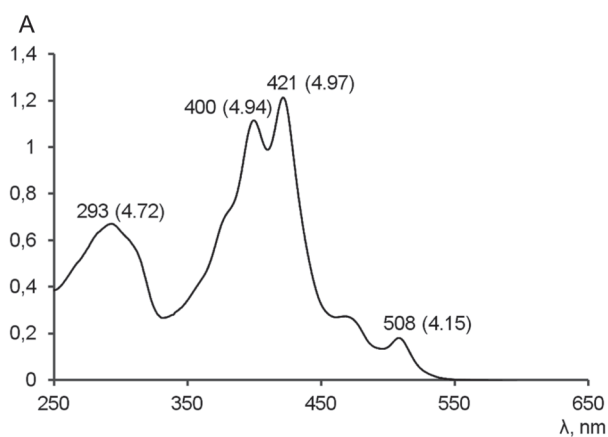
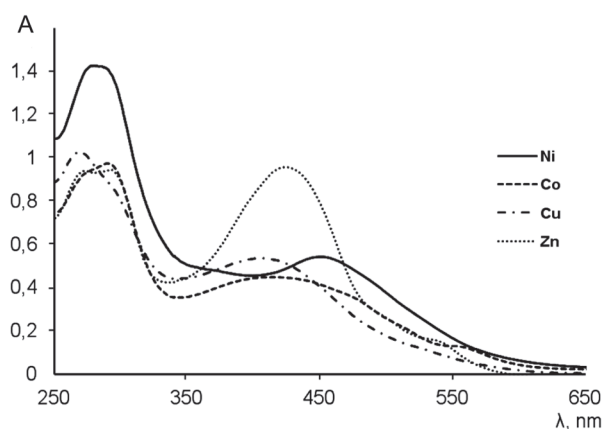


Figure 2. <sup>13</sup>C NMR spectrum for **3** in CDCl<sub>3</sub>.



**Figure 3.** UV-vis spectrum for **1** in  $\text{CHCl}_3$ , nm ( $\lg \epsilon$ ,  $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ).



**Figure 4.** UV-vis spectra for **1a-d** in  $\text{CHCl}_3$ .

with water and hot methanol upon filtration and further dried under vacuum.

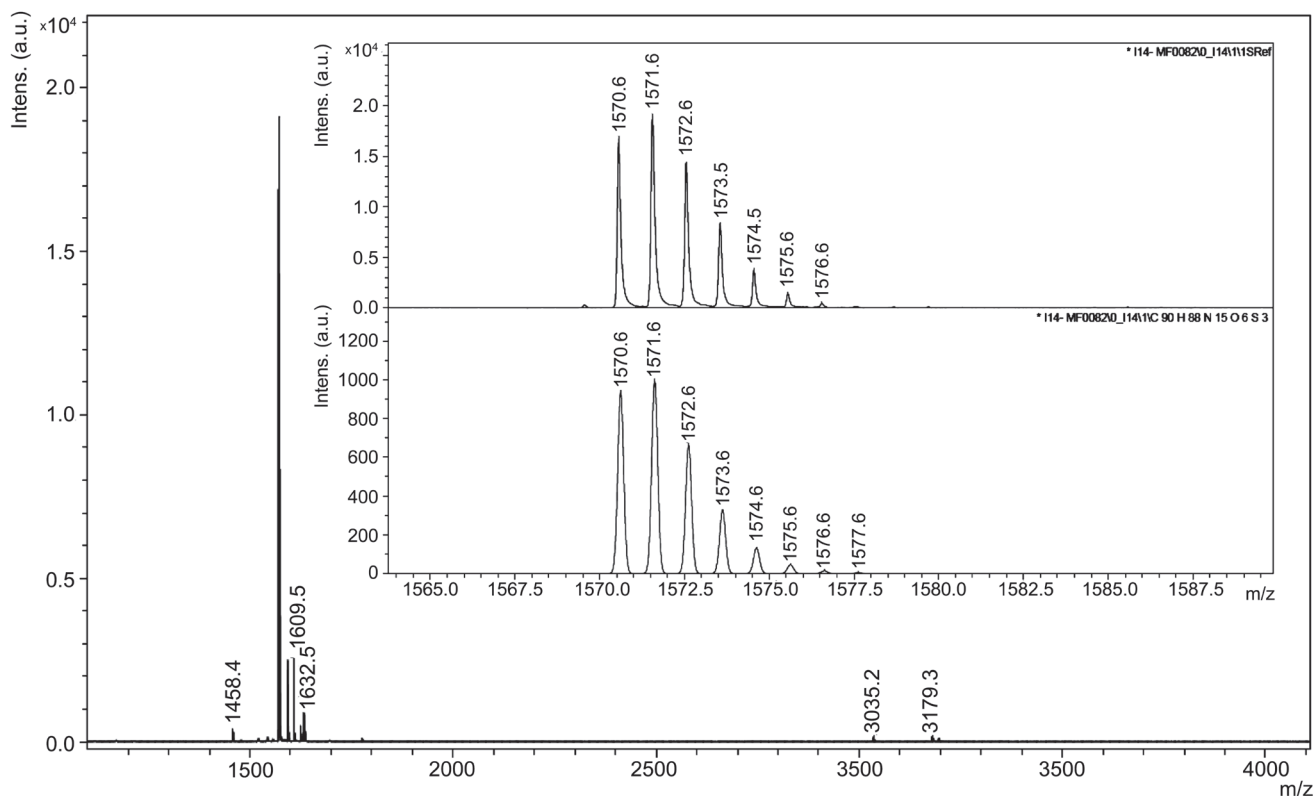
Compounds **1a-d** were characterized by mass-spectrometry, UV-Vis, and IR-spectroscopy. In the IR-spectra of **1a-d** no signals corresponding to vibrations of N-H bonds of inner coordination cavity were found. Electronic absorption spectra of metal complexes **1a-d** are shown below (Figure 4).

In the mass-spectra there are no signals, corresponding to  $[\text{Mc}+3\text{M}+3\text{X}]$ . Intense signals of molecular ions corresponding to  $[\text{Mc}+3\text{M}+\text{O}]^+$  (wherein Mc - ligand, M - metal atoms) were found in the spectra of compounds **1a-d**. We should note that we have previously observed this phenomenon. It's possible to assume that the cations where three metal atoms bond to one oxygen atom are formed as a result of harsh conditions of MALDI-TOF mass-experiment (Figure 5).

## Conclusions

A new hexa(4-*tert*-butylphenoxy) substituted trithia-dodecaaza[30]hexaphyrin was obtained by a reaction of 4,5-bis(4-*tert*-butylphenoxy)phthalonitrile and 2,5-diamino-1,3,4-thiadiazole in ethylene glycol, as well as its  $\text{Ni}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$  3:1 metallocomplexes. All the compounds were characterized by UV-Vis, IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy, mass-spectrometry and elemental analysis. High solubility in organic solvents of **1** and **1a-d** allows their purification by column chromatography and spectroscopic characterization.

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**Figure 5.** MALDI TOF MS spectrum for **1b**.

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