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Tetraanthraquinonoporphyrazines: III.[1] Synthesis and Physicochemical Properties of Metal Complexes of Hydroxy-Substituted Tetraanthraquinonoporphyrazines

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Abstract—Methods have been developed for the synthesis of metal complexes of hydroxy-substituted tetraanthraquinonoporphyrazines. The yield of the target products has been improved via complexation with the corresponding methoxy derivatives and subsequent hydrolysis of the methoxy groups. Some physicochemical properties of substituted 9,10-dioxo-9,10-dihydroanthracene-2,3-dicarboxylic acids and tetraanthraporphyrazine metal complexes derived therefrom have been studied.

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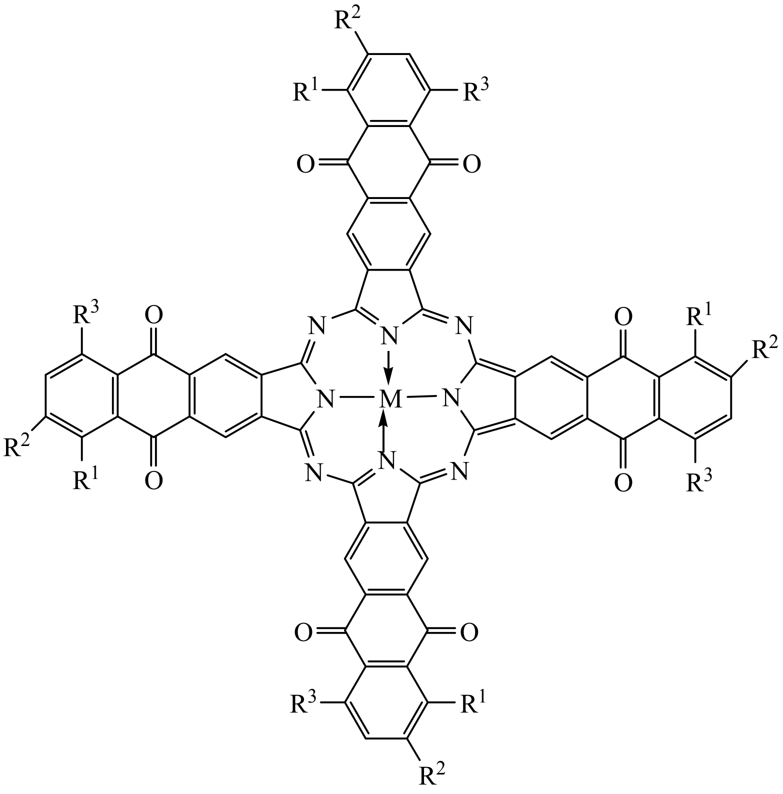
Extensive studies in the field of synthesis and properties of phthalocyanines and their metal complexes gave rise to a number of technically important products, such as dyes, redox catalysts, sensors, and liquid crystals [2–5]. Profound modification of the molecular structure of these compounds is expected to provide new data and practically useful materials. A unique set of physicochemical properties potentially intrinsic to substituted and fused phthalocyanines and their metal complexes determines persistent interest in these compounds, which may result in considerable extension of their application scope. Only a few published data are available on the synthesis and properties of tetraanthraquinonoporphyrazine metal complexes [1, 6–10]. Furthermore, most tetraanthraquinonoporphyrazine derivatives are insoluble in organic solvents and aqueous medium, which strongly restricts their detailed studies for applied purposes.

The present study was aimed at developing methods for the synthesis of metal complexes of tetraanthraquinonoporphyrazines (compounds **I–III**) having different numbers of hydroxy groups in combination with other substituents with a view to extend the series of their water-soluble derivatives (Scheme 1).

Metal complexes of tetraarenoporphyrazines are generally synthesized by template cyclotetramerization of *ortho*-dicarboxylic acids or their functional derivatives (amides, imides, or nitriles) in the presence of metal salts [1, 2, 6–10]. Therefore, the key step of our study was the synthesis of the corresponding 2,3-dicarboxy-substituted anthraquinones. It is known that 1,4-dihydroxyanthraquinone can be prepared by condensation of phthalic anhydride with hydroquinone in concentrated sulfuric acid using boric acid as catalyst. During the process the reaction mixture changes from cream-colored to brown due to formation of boron oxide chelate with quinizarin; the latter precipitates upon dilution of the reaction mixture with water and readily undergoes decomposition with formation of 1,4-dihydroxyanthraquinone on treatment with a hot dilute solution of a mineral acid or dilute alkali [11]. This procedure was used to synthesize 5,8-dihydroxy-9,10-dioxo-9,10-dihydroanthracene-2,3-dicarboxylic acid by reaction of pyromellitic dianhydride with hydroquinone (Scheme 2).

[†] Deceased.
[1] For communication II, see [1].

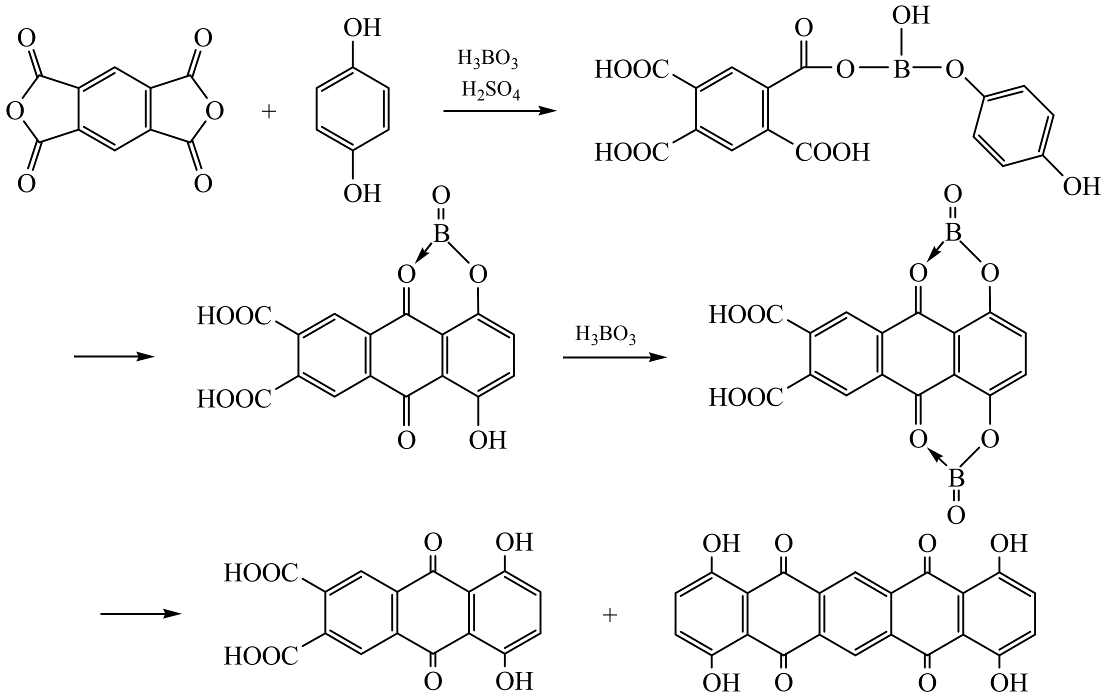
Scheme 1.



I–III

M = Cu, Co; **I**, $R^1 = R^3 = H$, $R^2 = OH$; **II**; $R^2 = H$, $R^1 = R^3 = OH$; **III**, $R^1 = R^3 = OH$, $R^2 = SO_3H$.

Scheme 2.



IV **V**

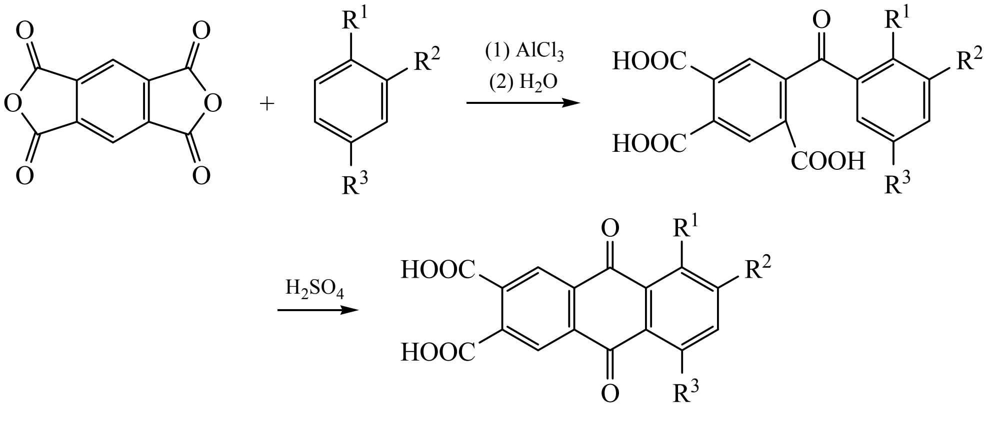
Apart from target product **IV**, 1,4,8,11-tetrahydroxypentacene-5,7,12,14-tetraone (**V**) was formed as impurity (Scheme 2). Our attempts to separate these compounds were unsuccessful. Therefore, dicarboxylic acid **IV** was obtained in a different way, by hydrolysis of 5,8-dimethoxy-9,10-dioxo-9,10-dihydroanthracene-2,3-dicarboxylic acid (**VII**) in aqueous alkali. Methoxy-substituted anthraquinones **VI** and **VII** were synthesized by acylation of anisole and 1,4-dimethoxybenzene, respectively, with pyromellitic anhydride according to the procedure described in [12] (Scheme 3), and their hydrolysis afforded the corresponding hydroxy derivatives **VIII** and **IX**. The acylation was carried out either using anisole as solvent or in heptane. Benzoyltrimellitic acids thus formed were converted into 2,3-dicarboxyanthraquinones by the action of 100% sulfuric acid.

It is known that introduction of sulfo groups into porphyrazine molecules makes them readily soluble in water and aqueous alkali [2]. Therefore, we also tried to obtain tetraanthraquinonoporphyrazine complexes containing sulfo groups in addition to hydroxy. According to [11], sulfonation of quinizarin with oleum occurs at the β-position. In fact, the sulfonation of 5,8-dimethoxy-9,10-dioxo-9,10-dihydroanthracene-2,3-dicarboxylic acid (**VII**) under analogous conditions gave 5,8-dimethoxy-9,10-dioxo-6-sulfo-9,10-dihydroan-hracene-2,3-dicarboxylic acid (**X**) (Scheme 4).

2,3-Dicarboxyanthraquinones **IV** and **VI**–**X** were identified on the basis of their elemental compositions and IR and electronic absorption spectra. Among these compounds, only monomethoxy derivative **VI** did not absorb in the visible region. The presence of absorption bands in the visible region of the electronic spectra of compounds **IV** and **VII**–**X** having two electron-donor substituents (methoxy or hydroxy groups) may be rationalized in terms of interaction of the latter with electron-withdrawing carbonyl groups (Fig. 1).

Methoxy-substituted anthracene-2,3-dicarboxylic acids **VI**, **VII**, and **X** were subjected to template cyclotetramerization with urea, ammonium chloride, and copper(II) or cobalt(II) acetate in the presence of ammonium molybdate to obtain tetraanthraquinonoporphyrazine complexes **XI**–**XIII**. When the corresponding hydroxy derivatives were used as initial com-

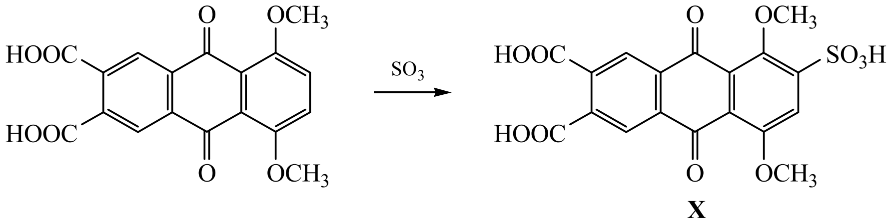
Scheme 3.



VI, VII

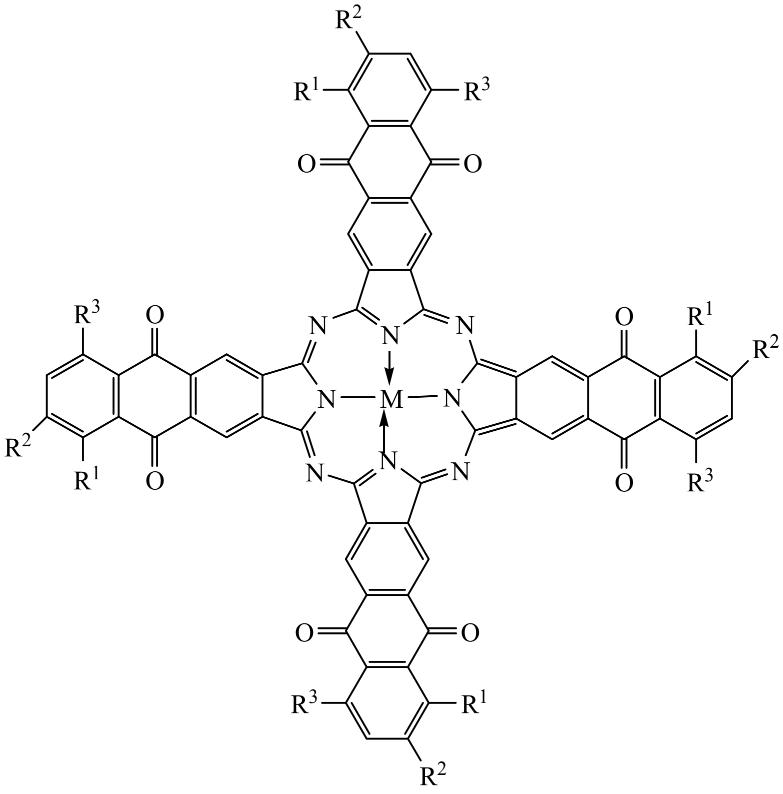
VI, $R^1 = R^3 = H$, $R^2 = OMe$; **VII**, $R^2 = H$, $R^1 = R^3 = OMe$.

Scheme 4.



X

Scheme 5.



XI–XIII

M = Cu (**a**), Co (**b**); **XI**, $R^1 = R^3 = H$, $R^2 = OMe$; **XII**, $R^2 = H$, $R^1 = R^3 = OMe$; **XIII**, $R^1 = R^3 = OMe$, $R^2 = SO_3H$.

pounds, the yield of metal porphyrazine complexes was lower (40–46%). Hydrolysis of the methoxy groups in complexes **XI**–**XIII** was performed at 60°C in 1% aqueous sodium hydroxide, and the yield of hydroxy-substituted complexes **I**–**III** reached 60–70% [13, 14] (Scheme 5).

Samples of complexes **I**–**III** obtained by the two methods had identical properties. They were isolated as blue to blue–green solids which were soluble in aqueous alkali, as well as in DMF and DMSO (except for **I** and **XII**). The complexes were purified by washing with concentrated hydrochloric acid and water, reprecipitation from concentrated sulfuric acid onto ice, and prolonged extraction with acetone (to remove impurities). Their structure was confirmed by elemental analysis and IR and electronic spectroscopy.

The IR spectra of substituted tetraanthraquinonoporphyrazines **I**–**III** and **XI**–**XIII** were analogous to the spectra of phthalocyanines with the difference that absorption bands typical of anthraquinone were present in the region 2800–2900 cm^{-1} [8]. The electronic spectra of these compounds in 1% aqueous sodium hydroxide displayed three absorption bands with their maxima at λ 340–349, 610–640, and 678–685 nm; analogous spectral patterns were observed for solutions in DMF (Table 1). The spectra of complexes **XI** and

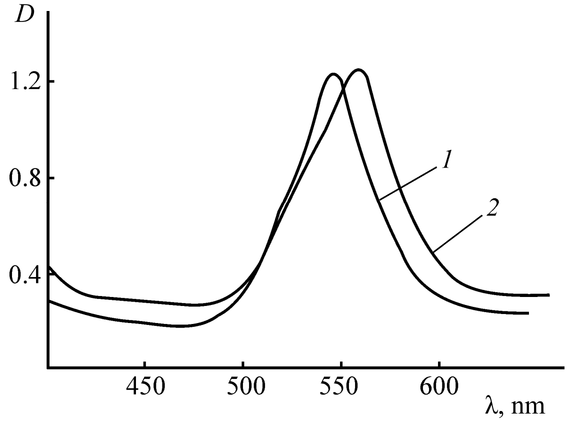


Fig. 1. Electronic absorption spectra of (*1*) 5,8-dimethoxy-9,10-dioxo-9,10-dihydroanthraquinone-2,3-dicarboxylic acid (**IV**) and (*2*) 5,8-dihydroxy-9,10-dioxo-9,10-dihydroanthraquinone-2,3-dicarboxylic acid (**IX**) in 1% aqueous sodium hydroxide.

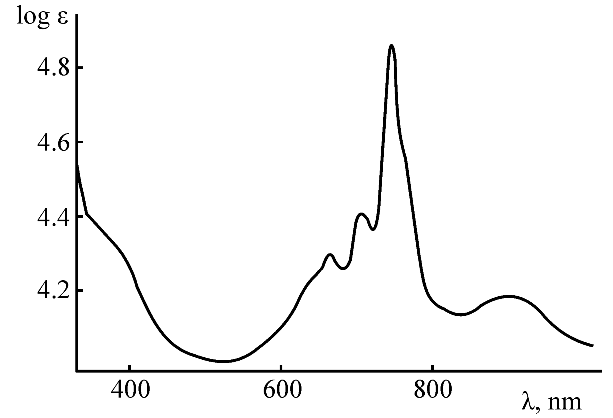


Fig. 2. Electronic absorption spectrum of complex **XIb** in H_2SO_4.

XII in DMF contained only two absorption bands at λ 350–354 and 685–691 nm. Presumably, the examined complexes in solution (except for **XI** and **I** in DMF) exist mainly as associates. As might be expected, fusion of 1,4-naphthoquinone fragments to phthalocyanine molecule leads to an appreciable red shift of the *Q* band.

The nature and number of substituents insignificantly affect the spectral pattern and position of absorption maxima in the examined solvents. Presumably, remote peripheral substituents exert a weak effect of on the electronic structure of the main chromophore, which is responsible for absorption in the visible region. The same applies to the spectra of these compounds in concentrated sulfuric acid. Protonation of the macroring induces a red shift of the long-wave maxima (by ~50 nm for the *Q* band), and the spectrum contains four bands. In addition to absorption maxima at λ 663–668, 703–708, and 744–746 nm, a weak diffuse absorption appears at λ 915–920 nm (Fig. 2). Comparison with the spectra of copper and cobalt phthalocyanines shows that fusion of substituted 1,4-naphthoquinone fragments reduces the magnitude of the red shift of the *Q* band. A probable reason is the effect of electron-withdrawing carbonyl groups, which reduces the basicity of the *meso*-nitrogen atoms. Possible protonation of carbonyl groups in concentrated sulfuric acid enhances this effect.

$$\underset{\textbf{XIa, XIb}}{\mathrm{MTAQPa(6\text{-}OCH_3)_4}} \xrightarrow[\text{(2) HCl}]{\text{(1) NaOH}} \underset{\textbf{Ia, Ib}}{\mathrm{MTAQPa(6\text{-}OH)_4}}$$

$$\underset{\textbf{XIIa, XIIb}}{\mathrm{MTAQPa(5,8\text{-}OCH_3)_4}} \xrightarrow[\text{(2) HCl}]{\text{(1) NaOH}} \underset{\textbf{IIa, IIb}}{\mathrm{MTAQPa(5,8\text{-}OH)_8}}$$

$$\underset{\textbf{XIIIa, XIIIb}}{\mathrm{MTAQPa(6\text{-}SO_3H)_4(5,8\text{-}OCH_3)_8}} \xrightarrow[\text{(2) HCl}]{\text{(1) NaOH}} \underset{\textbf{IIIa, IIIb}}{\mathrm{MTAQPa(6\text{-}SO_3H)_4(5,8\text{-}OH)_8}}$$

The solubility of the synthesized metal complexes in aqueous alkali makes it possible to test them as homogeneous catalysts in the oxidation of sulfur-containing compounds. This will be the subject of our further studies.

Table 1. Electronic absorption spectra of metal complexes of substituted tetraanthraquinonoporphyrazines

Comp. no.	M	λ_{max}, nm (log ε)
Ia	Cu	H_2SO_4: 667 (4.36), 704 (4.45), 745 (4.85); NaOH: 344, 638, 673; DMF: 354 (4.58), 624 (4.08), 691 (4.77)
Ib	Co	H_2SO_4: 665 (4.43), 704 (4.59), 746 (5.09); NaOH: 344, 643, 683; DMF: 355 (4.68), 625 (4.16), 693 (4.87)
IIa	Cu	H_2SO_4: 669 (4.31), 708 (4.48), 746 (4.90); NaOH: 638, 674; DMF: 352 (4.71), 625 (4.23), 695 (4.78)
IIb	Co	H_2SO_4: 668 (4.27), 705 (4.44), 746 (4.87); NaOH: 342, 643, 683; DMF: 352 (4.62), 624 (4.25), 694 (4.79)
IIIa	Cu	H_2SO_4: 669 (4.31), 708 (4.48), 746 (4.90); NaOH: 638, 674; DMF: 352 (4.71), 625 (4.23), 695 (4.78)
IIIb	Co	H_2SO_4: 668 (4.27), 705 (4.44), 746 (4.87); NaOH: 342, 643, 683; DMF: 352 (4.62), 624 (4.25), 694 (4.79)
XIa	Cu	H_2SO_4: 669 (4.25), 704 (4.42), 744 (4.86), 764 (4.53); DMF: 350, 685
XIb	Co	H_2SO_4: 669 (4.24), 704 (4.39), 744 (4.83), 764 (4.50); DMF: 347, 682
XIIa	Cu	H_2SO_4: 667 (4.33), 705 (4.46), 745 (4.89); DMF: 354, 691
XIIb	Co	H_2SO_4: 665 (4.98), 704 (5.11), 744 (5.50); DMF: 351, 689
XIIIa	Cu	H_2SO_4: 668 (4.37), 704 (4.49), 746 (4.89); NaOH: 340, 626
XIIIb	Co	H_2SO_4: 667 (4.26), 704 (4.43), 745 (4.84); NaOH: 340, 628

Table 2. Yields, melting points, and elemental analyses of 2,3-dicarboxyanthraquinone and its derivatives

Comp. no.	Yield, %	mp, °C	Found, %		Formula	Calculated, %	
			C	H		C	H
VI	88	348	62.3	3.2	$C_{17}H_{10}O_7$	62.6	3.1
VII	86	354	60.1	3.5	$C_{18}H_{12}O_8$	60.7	3.4
VIII	–	–	61.6	2.6	$C_{16}H_8O_7$	61.8	2.5
IX	84	296	58.2	2.6	$C_{16}H_8O_8$	58.6	2.5
X	44	350	49.5	2.9	$C_{18}H_{12}SO_{11}$	49.6	2.8

Table 3. Yields and elemental analyses of metal complexes of tetraanthraquinonoporphyrazines[a]

Comp. no.	Yield, %	Found, %			Formula	Calculated, %		
		C	H	N		C	H	N
Ia	38[b], 86[c]	62.3	2.3	10.8	$C_{64}H_{24}N_8O_{12}Cu$	62.2	2.3	10.7
Ib	44[b], 87[c]	62.6	2.3	10.8	$C_{64}H_{24}N_8O_{12}Co$	62.3	2.4	10.7
IIa	40[b], 82[c]	62.3	2.1	9.3	$C_{64}H_{24}N_8O_{16}Cu$	62.8	2.0	9.2
IIb	46[b], 87[c]	62.8	2.1	9.4	$C_{64}H_{24}N_8O_{16}Co$	63.0	2.0	9.2
IIIa	89	49.7	1.7	7.2	$C_{64}H_{24}N_8O_{28}S_4Cu$	49.8	1.6	7.3
IIIb	84	49.8	1.7	7.4	$C_{64}H_{24}N_8O_{28}S_4Co$	49.9	1.6	7.3
XIa	73	66.5	2.9	9.0	$C_{68}H_{32}N_8O_{12}Cu$	67.1	2.7	9.2
XIb	78	67.1	2.9	9.6	$C_{68}H_{32}N_8O_{12}Co$	67.4	2.7	9.8
XIIa	72	64.3	3.6	8.3	$C_{72}H_{48}N_8O_{16}Cu$	64.1	3.8	8.1
XIIb	82	64.5	3.6	8.4	$C_{72}H_{48}N_8O_{16}Co$	64.3	3.7	8.2
XIIa	83	51.9	2.9	6.7	$C_{72}H_{48}N_8O_{28}S_4Cu$	51.7	3.0	6.5
XIIIb	84	52.1	2.9	6.8	$C_{72}H_{48}N_8O_{28}S_4Co$	51.9	3.0	6.6

[a] In all cases samples were evacuated at 150°C. [b] From hydroxy anthraquinone. [c] From methoxy anthraquinone.

EXPERIMENTAL

Acylation of anisole. Anhydrous aluminum chloride, 16.12 g (0.119 mol), was added under vigorous stirring to a mixture of 10.0 g (0.046 mol) of pyromellitic dianhydride and 25 ml of anisole. The mixture was stirred for 2 h at room temperature, heated on a water bath to 75–80°C over a period of 4 h, and kept for 10 h at that temperature. The mixture was cooled, 50 ml of ice water was carefully added, and the mixture was kept for 30 min. The resulting suspension was treated under stirring with a hot solution of sodium carbonate, and the precipitate of aluminum hydroxide was filtered off. The aqueous–organic filtrate was treated with hydrochloric acid to pH 3–4 and left to stand for 5 h. The precipitate was filtered off, washed with water until neutral washings, and dried at 60–80°C.

Acylation of 1,4-dimethoxybenzene. A mixture of 10.0 g (0.046 mol) of pyromellitic dianhydride and 7.1 g (0.051 mol) of 1,4-dimethoxybenzene in 20 ml of heptane was heated to 50°C, 16.12 g (0.119 mol) of anhydrous aluminum chloride was added, and the mixture was heated for 3 h under reflux. The solvent was distilled off, and the residue was heated for 6 h at 120–130°C. The mixture was cooled, 50 ml of water and 10 ml of concentrated hydrochloric acid were carefully added, and the mixture was stirred for 12 h. The resulting suspension was filtered, and the precipitate was washed with hot water and heated for 30–40 min in a boiling 10% solution of sodium carbonate. The hot suspension was filtered, and the precipitate was treated as described above 3–4 times more. The filtrate was acidified with hydrochloric acid to pH 4 and cooled to 10–15°C, and the precipitate was filtered off, washed with water until neutral washings, and dried at 80°C.

9,10-Dioxo-9,10-dihydroanthracene-2,3-dicarboxylic acids VI and VII (*general procedure*). The corresponding benzoyltrimellitic acid, 5.0 g, was added over a period of 15 min under vigorous stirring to 20.0 ml of 100% sulfuric acid heated to 130°C, and the mixture was heated to 150°C and kept for 5 h at that temperature. The mixture was then poured into 200 ml of water under stirring, the resulting suspension was filtered, the precipitate was washed with water until neutral washings and dissolved in 100 ml of 10% aqueous sodium carbonate. The solution was filtered, the filtrate was acidified with hydrochloric acid to pH 4, and the precipitate was filtered off and washed with water until the washings no longer contained chloride ions. This procedure was repeated twice, and the product was dried at 100°C.

5,8-Dihydroxy-9,10-dioxo-9,10-dihydroanthracene-2,3-dicarboxylic acid (IV). A 200-ml three-necked flask equipped with a stirrer was charged with a ground mixture of 10.1 g (0.092 mol) of hydroquinone, 10.0 g (0.046 mol) of pyromellitic dianhydride, and 14.5 g (0.23 mol) of boric acid, 70 ml of 100% sulfuric acid was added, and the mixture was thoroughly stirred and heated for 3 h at 140–150°C. The mixture was then heated for 3 h at 160–170°C and poured while hot into 400 ml of water under vigorous stirring. The mixture was heated to the boiling point and filtered while hot. The precipitate was treated once more with 400 ml of boiling water, filtered off, treated with 20 ml of a 1% solution of sodium hydroxide, and filtered off. The procedure was repeated until the product no longer dissolved. The filtrates were combined and neutralized with hydrochloric acid, and the precipitate was filtered off and washed with water until neutral washings. The product was dried at 80°C and extracted with glacial acetic acid in a Soxhlet apparatus over a period of 20 h. The extract was evaporated, and the residue was dried at 100°C.

6-Hydroxy-9,10-dioxo-9,10-dihydroanthracene-2,3-dicarboxylic acid (VIII) and 5,8-dihydroxy-9,10-dioxo-9,10-dihydroanthracene-2,3-dicarboxylic acid (IV) (*general procedure*). A mixture of 0.20 g of methoxy derivative **VI** or **VII** and 10 ml of 1% aqueous sodium hydroxide was ground and heated for 40–50 min on a water bath. The mixture was acidified with hydrochloric acid to pH 3–4, and the precipitate was filtered off, washed with water until the washings no longer contained chloride ions, and dried at 100°C.

5,8-Dimethoxy-9,10-dioxo-6-sulfo-9,10-dihydroanthracene-2,3-dicarboxylic acid (X). 5,8-Dimethoxy-9,10-dioxo-9,10-dihydroanthracene-2,3-dicarboxylic acid (**VII**), 2.00 g (0.07 mol), was added under stirring to 16 ml of 20% oleum heated to 120–140°C, and the mixture was kept for 6 h at that temperature. The mixture was cooled and poured onto ice, and the precipitate was filtered off, washed with 5% aqueous HCl until the absence of sulfate ions, and dried at 100°C.

The yields, melting points, and elemental analyses of compounds **VI–X** are given in Table 2.

Metal complexes of substituted tetraanthraquinonoporphyrazines *(general procedures)*. *a*. A quartz ampule was charged with a mixture of 0.60 mmol of the corresponding substituted 2,3-dicarboxyanthraquinone, 4.00 mmol (0.24 g) of urea, 0.18 mmol of copper(II) (0.036 g) or cobalt(II) acetate (0.038 g), 0.40 mmol (0.02 g) of ammonium chloride, and 0.01 mmol (0.002 g) of ammonium molybdate. The mixture was slowly (over a period of 1 h) heated to 180°C, kept for 3 h at that temperature, cooled, ground, transferred onto a Schott filter, and washed with 5% aqueous HCl and water until evaporation of a drop of the filtrate on a glass plate left no solid residue. The product was dried at 100°C, reprecipitated from concentrated sulfuric acid, extracted with acetone in a Soxhlet apparatus over a period of 10 h, and dried at 100°C.

b. A mixture of 0.20 g of thoroughly ground complex **XI–XIII** and 10 ml of 1% aqueous sodium hydroxide was heated for 40–50 min on a water bath. The solution was acidified with hydrochloric acid to pH 3–4, and the precipitate was filtered off, washed with water until the washings no longer contained chloride ions, and dried at 100°C.

The yields, elemental analyses, and electronic absorption spectra of complexes **I–III** and **XI–XIII** are given in Table 3.

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