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COORDINATION COMPOUNDS

Synthesis of *ms*- and β-Substituted Ruthenium(II) Porphyrinates

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Abstract—The reactions of 5,10,15,20-tetraphenylporphine, 2,3,7,8,12,13,17,18-octaethylporphine, and tetra(4-methoxyphenyl)porphine with $Ru_3(CO)_{12}$ in boiling phenol were studied by spectrophotometry. The following compounds were synthesized and identified: $Ru^{2+}(CO)(H_2O)$ 5,10,15,20-tetraphenylporphyrinate, $Ru^{2+}(CO)(H_2O)$ 2,3,7,8,12,13,17,18-octaethylporphyrinate, $Ru^{2+}(CO)(Py)$ 2,3,7,8,12,13,17,18-octaethylporphyrinate, and $Ru^{2+}(CO)(H_2O)$ tetra(4-methoxyphenyl)porphyrinate. The strong electronic effect of the substituents on the reactivity of the tetrapyrrole cycle during the formation of the corresponding porphyrinates was established.

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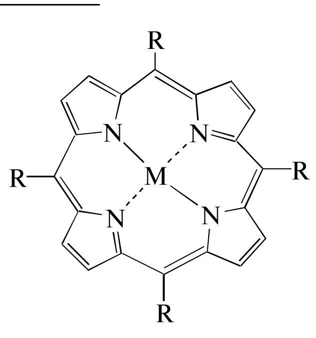
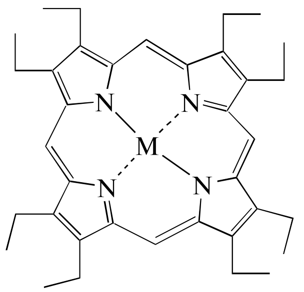
Porphyrins and related tetrapyrrole macrocycles in the composition of metal complexes are known to manifest photochromic and catalytic properties. Porphyrin complexes with ruthenium are of special interest for the design of controlled functional materials [1, 2].

There are described syntheses of $Ru^{2+}(CO)(Py)$ tetraphenylporphyrinate and $Ru^{2+}(CO)(Py)$ octaethylporphyrinate by the reactions of 5,10,15,20-tetraphenylporphine (**I**) and 2,3,7,8,12,13,17,18-octaethylporphine (**II**) with $Ru_2(CO)_9$ and $Ru_3(CO)_{12}$ in pyridine [3, 4]. Benzene, toluene, and acetic and propionic acids were also used as solvents. In all cases, prolong heating (22 to 60 h) is required. The use of 2-(2-methoxyethoxy)ethanol and decalin as solvents shortens the reaction time to 4–5 h [4]. It was shown that $Ru^{2+}(CO)(CH_3OH)$ *meso*-tetra(benzo-15-crown-5)porphyrinate was formed from the corresponding porphyrin ligand and $Ru_3(CO)_{12}$ in boiling 1,2,4-trichlorobenzene for 5 min [5]. Collman et al. [6] synthesized $Ru^{2+}(CO)(CH_3OH)$ tetraphenylporphyrinate and $Ru^{2+}(CO)(CH_3OH)$ octaethylporphyrinate from ligands **I** and **II** with $RuCl_3 \cdot H_2O$ in boiling 2-(2-methoxyethoxy)ethanol in a carbon monoxide atmosphere. The reaction of compound **I** with K_2RuO_4 (1 : 30 mol/mol) in boiling phenol yielded Ru^{4+} (diphenoxo)tetraphenylporphyrinate [7], which underwent no substitution at the extra ligand during purification on alumina. However, no reaction time was specified [7], and Ru^{2+} tetra(4-methoxyphenyl)porphyrinate was not described.

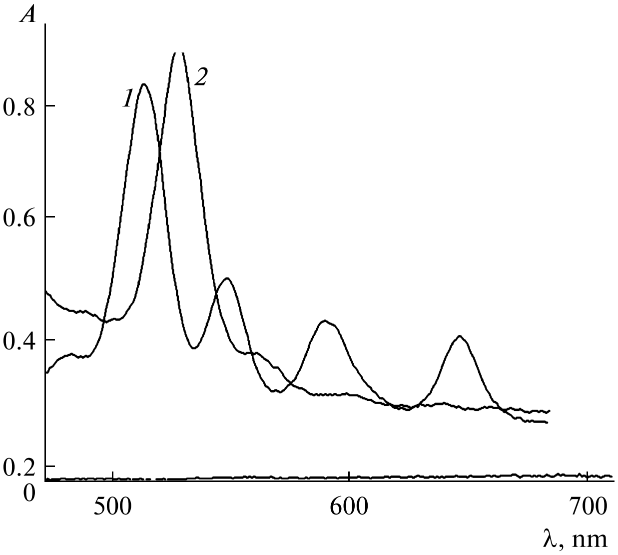
For the purpose of creating porphyrin-containing photochromic systems capable of giving response to an external action, we developed efficient methods for the synthesis of β- and *ms*-substituted Ru^{2+} porphyrinates and studied the influence of the chemical modification of the molecule on the reactivity of the tetrapyrrole cycle toward $Ru_3(CO)_{12}$ in boiling phenol.



$M = H_2$, $R = C_6H_5$ (**I**),
$M = H_2$, $R = C_6H_4–4OCH_3$ (**III**),
$M = Ru^{2+}(CO)(H_2O)$, $R = C_6H_5$ (**IV**),
$M = Ru^{2+}(CO)(H_2O)$, $R = C_6H_5–4OCH_3$ (**VII**),
$M = Zn^{2+}$, $R = C_6H_5$ (**VIII**).



$M = H_2$ (**II**),
$M = Ru^{2+}(CO)(H_2O)$ (**V**),
$M = Ru^{2+}(CO)(Ry)$ (**VI**).



Electronic absorption spectra in chloroform of (*1*) compound **I** and (*2*) compound **IV**.

EXPERIMENTAL

Porphyrin ligands **I–III** were synthesized using a known method [8]. The solvents were purified according to a described procedure [9]. The course of complex formation of the metal cation with the porphyrin ligand was monitored by spectrophotometry and thin layer chromatography (TLC) on Silufol (G/UV_{254}) plates using a chloroform–ethanol (20 : 1) system as an eluent. The spectrophotometric study was as follows: samples of equal volumes were taken from the reaction mixture at certain time intervals, diluted with the same amount of dimethylformamide, and transferred to an optical cell. Electronic absorption spectra (figure) were recorded on a Cary-100 spectrophotometer at 298 K. IR spectra were measured on an Avatar 360 FT-IR ESP spectrometer as KBr pellets. ^{1}H NMR spectra were obtained on a Bruker AC-200 instrument in $CDCl_3$. TLC was carried out on Silufol (G/UV_{254}) plates. Elemental analysis was performed with a Flash EA 1112 analyzer. The elemental analysis data correspond completely to the presented structures of the compounds synthesized.

$Ru^{2+}(CO)(H_2O)$ 5,10,15,20-Tetraphenylporphyrinate (IV). A mixture of porphyrin **I** (0.05 g, 0.081 mmol) and $Ru_3(CO)_{12}$ (0.035 g, 0.054 mmol) was refluxed in phenol (5 g) for 1 h. The melt was cooled, dissolved in dimethylformamide (20 mL), and poured into water. The precipitate formed was filtered off and washed with hot water. The residue was doubly chromatographed on alumina with chloroform elution. The yield of compound **IV** after column chromatography was 0.045 g (0.056 mmol, 73%), $R_f = 0.81$. IR (cm^{-1}): 2929 w, 1958 s, 1650 w, 1596 m, 1521 w, 1430 w, 1351 m, 1306 w, 1165 w, 1070 m, 1009 s, 795 m, 753 s, 703 m, 670 w, 520 w, 445 w, 405 w. ^{1}H NMR (δ, ppm): 8.65 d (8H), 8.05 d (8H), 8.21 t (8H), 7.70 t (4H), 0.15 s (2H).

Analogous syntheses were carried out to obtain $Ru^{2+}(CO)(H_2O)$ 2,3,7,8,12,13,17,18-octaethylporphyrinate (**V**) and $Ru^{2+}(CO)(H_2O)$ tetra(4-methoxyphenyl)porphyrinate (**VI**).

$Ru^{2+}(CO)(H_2O)$ 2,3,7,8,12,13,17,18-Octaethylporphyrinate (V) was synthesized from porphyrin **II** (0.05 g, 0.093 mmol) and $Ru_3(CO)_{12}$ (0.04 g, 0.06 mmol). The reaction time was 3 min. The yield of compound **V** after column chromatography on silica gel (eluent $CHCl_3$) was 0.046 g (0.068 mmol, 72%), $R_f = 0.79$. IR (cm^{-1}): 2960 s, 2926 s, 2856 m, 1924 s, 1727 w, 1681 w, 1631 w, 1539 w, 1454 m, 1385 m, 1356 m, 1309 w, 1266 m, 1231 m, 1182 w, 1149 s, 1103 m, 1059 m, 1026 m, 985 m, 949 w, 841 w, 7523 m, 736 m, 722 m, 468 w, 408 w. ^{1}H NMR (δ, ppm): 9.95 s (4H), 4.05 q (16H), 1.95 t (24H), 0.08 s (2H).

$Ru^{2+}(CO)(Py)$ 2,3,7,8,12,18-Octaethylporphyrinate (VI). Complex **V** (0.02 g) was dissolved in pyridine (7 mL) and refluxed for 5 min. The reaction mixture was cooled and chromatographed on silica gel using a $CHCl_3$–Py (10 : 1) system as an eluent. The yield of compound **VI** was 0.015 g (0.02 mmol, 70%), $R_f =$ 0.75. ^{1}H NMR (δ, ppm): 9.80 s (4H), 3.95 q (16H), 1.88 t (24H), 5.85 m (2H) (γ-H_{py}), 4.90 m (4H) (β-H_{Py}), 2.25 br. s (4H) (α-H_{Py}).

$Ru^{2+}(CO)(H_2O)$ Tetra(4-methoxyphenyl)porphyrinate (VII) was synthesized from porphyrin **III** (0.05 g, 0.068 mmol) and $Ru_3(CO)_{12}$ (0.029 g, 0.045 mmol). The reaction time was 8 min. The yield of compound **VI** after column chromatography on alumina (eluent $CHCl_3$) was 0.046 g (0.053 mmol, 76%), $R_f = 0.73$. IR (cm^{-1}): 2927 w, 2852 w, 2058 w, 2040 w, 1938 s, 1606 m, 1574 w, 1528 m, 1511 s, 1464 s, 1434 s, 1410 w, 1350 s, 1304 w, 1287 w, 1246 s, 1175 s, 1075 s, 1007 s, 809 m, 796 m, 717 w, 673 w, 610 w, 467 s, 408 w. ^{1}H NMR (δ, ppm): 8.7 d (8H), 8.1 m (16H), 4.1 s (12H), 0.05 s (2H).

RESULTS AND DISCUSSION

It is known [7, 10] that metal ions in oxidation states lower than the maximum values are formed in a reductive medium (phenol). The complex formation rate with ruthenium carbonyl in phenol increases by about eight times on going from compound **I** to its tetra(4-methoxy)-substituted derivative **III**. A similar example for the high-performance (5 min) synthesis of $Ru^{2+}(CO)(CH_3OH)$ *meso*-tetra(benzo-15-crown-5)porphyrinate has already been described [5]. β-Substituted octaethylporphine coordinates to $Ru_3(CO)_{12}$ 20 times more rapidly than *ms*-substituted tetraphenylporphine. This indicates that the coordination interaction between the metal cation and the nitrogen atoms of porphyrin makes the determining contribution to the energy of the transition state during complex formation. The electron-donating *n*-methoxy groups of the phenyl fragments of porphyrin **III** and

Electronic absorption spectra of the porphyrin ligands and ruthenium and zinc porphyrinates

Compound	Solvent	Band I λ, nm (logε)	Band II λ, nm (logε)	Bands III, IV, V λ, nm (logε)	Soret band λ, nm (logε)	Source
I	C_5H_5N	646 (3.71)	591 (3.71)	549 (3.96) 515 (4.27)	420 (5.73)	[12]
I-Ru^{2+}(CO)(CH$_3$OH)	C_6H_6		532		412	[6]
I-Ru^{2+}(CO)(H$_2$O) (IV)	$CHCl_3$	562 sh	529 (4.30)		411 (5.31)	
II	C_6H_6	623 (3.79)	596 (3.18)	568 (3.83) 530 (4.02) 497 (4.15)	399 (5.21)	[12]
II-Ru^{2+}(CO)(Py)	CH_2Cl_2	545 (4.39)	518 (4.20)		396 (5.37)	[3]
II-Ru^{2+}(CO)(CH$_3$OH)	C_6H_6	549 (4.38)	517 (4.06)		393 (5.16)	[6]
II-Ru^{2+}(CO)(H$_2$O) (V)	$CHCl_3$	548 (4.34)	516 (4.11)		393 (5.24)	
II-Ru^{2+}(CO)(Py) (VI)	C_6H_6	550 (4.37)	518 (4.16)		396 (5.37)	
II-Ru^{2+}(Py)$_2$	C_6H_6	521 (4.58)	495 (4.17)	450 (4.20)	395 (5.01)	[11]
III	C_6H_6	651 (3.81)	598 (3.82)	554 (4.01) 517 (4.13)	422 (5.33)	
VII	$CHCl_3$	567 (3.94)	532 (4.34)		415 (5.34)	
VIII	$CHCl_3$	597 (3.99)	558 (4.36)		420 (5.19)	[8]

the β-ethyl substituents (compound **II**) enhance the coordination interaction of the metal cation with porphyrin by increasing the electron density on the tertiary nitrogen atoms of the macrocycle.

The methods we developed for the synthesis of ruthenium porphyrinates in boiling phenol substantially simplify the synthesis compared to the state-of-the-art methods [3, 4, 6]. In particular, the time of formation of Ru^{2+} tetraphenylporphyrinate and Ru^{2+} octaethylporphyrinate in phenol is one to two orders of magnitude shorter than is the syntheses of the corresponding compounds in pyridine [3, 4] and 2-(2-methoxyethoxy)ethanol [6].

The electronic absorption spectra of the synthesized ruthenium porphyrinates **IV**–**VII** agree well with the literature data (table). The hypsochromic shift of the bands in the spectra of ruthenium porphyrinates **IV**–**VII** compared to those of the porphyrinates containing the metal ion with the closed electronic shell (e.g., Zn^{2+}) is due to the strong π-dative interaction of the d_π–$e_g(\pi^*)$ type between the metal ion and the porphyrin macrocycle.

The IR spectrum of compound **IV** contains an intense band at 1958 cm^{-1} corresponding to the stretching vibrations (CO) of compounds **V** and **VII** at 1924 and 1939 cm^{-1}, respectively. Similar bands are observed in the IR spectra of **I**-Ru^{2+}(CO)(CH$_3$OH) and **II**-Ru^{2+}(CO)(CH$_3$OH) at 1930 and 1928 cm^{-1}, respectively [6]. These bands are not observed in the spectra of porphyrin ligands **I**–**III**.

It was shown for Ru^{2+}(CO)(H$_2$O) octaethylporphyrinate that pyridine easily substitutes for a water molecule. More severe conditions are required to substitute pyridine for the second extra ligand (CO) [11].

In the ^{1}H NMR spectrum of the synthesized Ru^{2+}(CO)(Py) octaethylporphyrinate (**VI**), the signals of Py protons appear at 5.85–2.25 ppm. The signals of protons of coordinated water lie in a high field (~0.08 ppm).

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