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Synthesis and Spectral Properties of *meso*-Substituted Ni^{2+} Octaalkylporphyrinates

N. V. Chizhova, O. V. Mal'tseva, and N. Zh. Mamardashvili

Krestov Institute of Solution Chemistry, Russian Academy of Sciences, ul. Akademicheskaya 1, Ivanovo, 153045 Russia
e-mail: nvc@isc-ras.ru

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Abstract—Nickel(II) 3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrinate and its 5,15-diaza, -diphenyl, and -di(4-bromophenyl) derivatives have been synthesized by the reaction of nickel(II) chloride with corresponding tetrapyrrole ligands in dimethylformamide.

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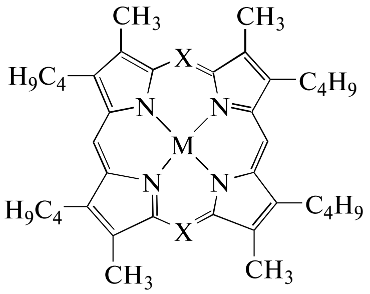
Palladium and nickel complexes with porphyrins are widely used as molecular thermometers, efficient sensors, and molecular switches [1, 2].

Previously, palladium porphyrinates have been synthesized by the complexation reaction of Pd^{2+} cation with 3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphine (**I**) and its 5,15-diaza (**II**), -diphenyl (**III**), and -di(4-bromopnenyl) (**IV**) derivatives in dimethylformamide (DMF) [3].

The present work has focused on the development of efficient methods of synthesis of nickel complexes with octaalkylporphyrins **I**–**IV**. The complexation reactions of nickel(II) chloride with ligands **I**–**IV** in boiling DMF have been studied. A significant difference between the electronic absorption spectra of the initial porphyrin ligands and the resulting nickel porphyrinates (figure) enabled the use of the spectrophotometric method for studying the reactions. Optimal conditions for the synthesis of nickel 3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphinate (**V**) and its 5,15-diaza (**VI**), -diphenyl (**VII**), and -di(4-bromophenyl) (**VIII**) derivatives have been found and spectral properties of the complexes have been studied.



M =Pd, X = CH (**I**),
M = Pd, X = N (**II**),
M = Pd, X = C-C_6H_5 (**III**),
M = Pd, X = C-4-BrC_6H_4 (**IV**),
M = Ni, X = CH (**V**),
M = Ni, X = N (**VI**),
M = Ni, X = C-C_6H_5 (**VII**),
M = Ni, X = C-4-BrC_6H_4 (**VIII**).

EXPERIMENTAL

Porphyrin ligands **I**–**IV** were synthesized as described in [4]. Chemically pure grade DMF and $CHCl_3$ were used as purchased. Chemically pure grade nickel(II) chloride was annealed at 200°C for 4 h. The course of the complexation reaction of metal cation with the porphyrin ligand was monitored by spectrophotometry and thin-layer chromatography (TLC). The spectrophotometric study procedure was as follows: at definite time intervals, equal volumes of the reaction mixture were sampled and dissolved in a definite amount of DMF. The resulting solution was placed in a cell. The electronic absorption spectra were recorded on a Cary-100 spectrophotometer at room temperature. TLC analysis was carried out on Silufol (G/UV_{254}) plates, elution with a 1 : 1 hexane–chloroform mixture. The ^1H NMR spectra were recorded on a Bruker AV III-500 spectrometer in deuteriochloroform. The IR spectra were recorded on an Avatar 360-FT-IR-ESP spectrophotometer as KBr pellets. Elemental analysis was carried out on a Flash EA 1112 analyzer.

Nickel(II) 3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrinate (V). A mixture of 0.05 g (0.085 mmol) of porphyrin **I** and 0.11 g (0.85 mmol) of $NiCl_2$ in 30 mL of DMF was heated to boiling and heated under reflux for 10 min, then cooled (a water–ice–salt mixture), and poured into water. The deposited precipitate was filtered off, washed with water, and chromatographed on alumina (elution with a 1 : 1 hexane–chloroform mixture) The yield of complex **V** was 0.025 g (0.038 mmol, 45%). $R_f = 0.74$.

For $NiC_{40}N_4H_{52}$ anal. calcd. (%): C, 74.19; N, 8.66; H, 8.09.

Found (%): C, 74.12; N, 8.62; H, 8.04.

^{1}H NMR (δ, ppm, $CDCl_3$): 9.79 (s, 4H, *ms*-H), 2.90 (s, 12H, CH_3), 2.98 (t, 8H, $\underline{CH_2}CH_2CH_2CH_3$), 1.60 (quint, 8H, $CH_2\underline{CH_2}CH_2CH_3$), 1.28 (sext, 8H, $CH_2CH_2\underline{CH_2}CH_3$), 0.90 (t, 12H, $CH_2CH_2CH_2\underline{CH_3}$).

IR (cm^{-1}): 3057 w, 2924 w, 2852 w, 1807 w, 1634 m, 1591 m, 1565 m, 1459 m, 1429 m, 1350 s, 1315 w, 1231 w, 1207 w, 1159 w, 1126 w, 1070 m, 1036 m, 1004 s, 866 w, 833 w, 797 s, 752 s, 710 m, 648 w, 486 w, 460 w.

Porphyrinates **VI**, **VII**, and **VIII** were synthesized and isolated analogously.

Nickel(II) 3,7,13,17-tetramethyl-2,8,12,18-tetrabutyl-5,15-diazaporphyrinate (VI). A mixture of 0.05 g of porphyrin **II** and 0.11 g of $NiCl_2$ (1 : 10 molar ratio) in 60 mL of DMF was heated to boiling and heated under reflux for 1 min. The yield was 0.024 g (0.037 mmol, 44%). $R_f = 0.75$.

For $NiC_{38}N_6H_{50}$ anal. calcd. (%): C, 70.26; N, 12.94; H, 7.76.

Found (%): C, 70.20; N, 12.89; H, 7.71.

^{1}H NMR (δ, ppm, $CDCl_3$): 9.79 (s, 4H, *ms*-H), 3.54 (s, 12H, CH_3), 3.96 (t, 8H, $\underline{CH_2}CH_2CH_2CH_3$), 1.84 (quint, 8H, $CH_2\underline{CH_2}CH_2CH_3$), 1.75 (sext, 8H, $CH_2CH_2\underline{CH_2}CH_3$), 0.92 (t, 12H, $CH_2CH_2CH_2\underline{CH_3}$).

IR (cm^{-1}: 3032 w, 2999 w, 2927 w, 2833 w, 1607 s, 1574 w, 1549 w, 1507 s, 1463 m, 1438 m, 1409 w, 1353 s, 1288 m, 1248 s, 1175 s, 1106 w, 1075 w, 1027 m, 1003 s, 849 w, 802 m, 786 w, 714 w, 639 w, 608 w, 540 w.

Nickel(II) 3,7,13,17-tetramethyl-2,8,12,18-tetrabutyl-5,15-diphenylporphyrinate (VII). A mixture of 0.05 g of porphyrin **III** and 0.087 g of $NiCl_2$ (1 : 10 molar ratio) in 50 mL of DMF was heated to boiling and heated under reflux for 1 min. The yield was 0.044 g (0.055 mmol, 82%). $R_f = 0.78$.

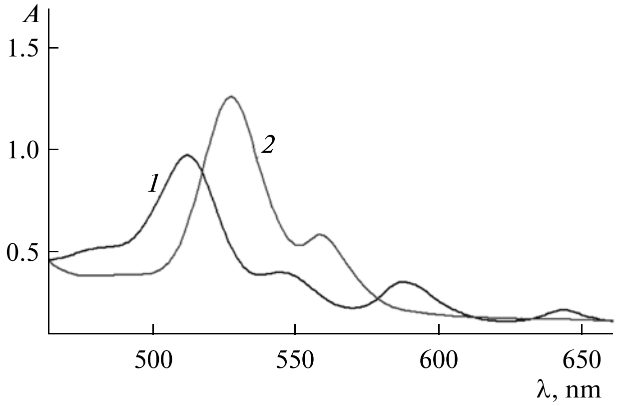
For $NiC_{52}N_4H_{60}$ anal. calcd. (%): C, 78.09; N, 7.01; H, 7.56.

Found (%): C, 78.02; N, 6.96; H, 7.53.

^{1}H NMR (δ, ppm, $CDCl_3$): 10.17 (s, 2H, *ms*-H), 8.04 (d, 4H, Aryl-*ortho*), 7.93 (t, 4H, Aryl-*meta*), 7.69 (t, Aryl-*para*), 2.98 (s, 12H, CH_3), 2.90 (t, 8H, $\underline{CH_2}CH_2CH_2CH_3$), 1.16 (quint, 8H, $CH_2\underline{CH_2}CH_2CH_3$), 1.12 (sext, 8H, $CH_2CH_2\underline{CH_2}CH_3$), 0.89 (t, 12H, $CH_2CH_2CH_2\underline{CH_3}$).

IR (cm^{-1}): 3230 w, 3068 w, 2959 s, 2918 s, 2868 m, 2849 m, 1738 w, 1667 w, 1569 w, 1537 w, 1453 m, 1393 m, 1311 w, 1263 m, 1232 m, 1147 m, 1108 m, 1058 m, 1024 m, 988 m, 934 w, 831 m, 756 w, 729 m, 709 m, 612 w, 515 w, 424 w.

Nickel(II) 3,7,13,17-tetramethyl-2,8,12,18-tetrabutyl-5,15-bis(4-bromophenyl)porphyrinate (VIII). A mixture of 0.05 g of porphyrin **IV** and 0.072 g of $NiCl_2$ (1 : 10 molar ratio) in 60 mL of DMF was heated to boiling and heated under reflux for 3 min. The yield was 0.04 g (0.042 mmol, 75%). $R_f = 0.78$.



Electronic absorption spectrum of (*1*) porphyrin **I** and (*2*) Ni^{2+} porphyrinate **V** in chloroform.

For $NiC_{52}N_4H_{58}Br_2$ anal. calcd. (%): C, 65.22; N, 5.85; H, 6.10.

Found (%): C, 65.16; N, 5.78; H, 6.05.

^{1}H NMR (δ, ppm, $CDCl_3$): 10.10 (s, 2H, *ms*-H), 7.84 (d, 4H, Aryl-*ortho*), 7.75 (d, 4H, Aryl-*meta*), 2.96 (s, 12H, CH_3), 2.88 (t, 8H, $\underline{CH_2}CH_2CH_2CH_3$), 1.27 (quint, 8H, $CH_2\underline{CH_2}CH_2CH_3$), 1.09 (sext, 8H, $CH_2CH_2\underline{CH_2}CH_3$), 0.86 (t, 12H, $CH_2CH_2CH_2\underline{CH_3}$).

IR (cm^{-1}): 2923 m, 2853 w, 1634 m, 1604 m, 1570 m, 1485 m, 1409 s, 1351 s, 1287 w, 1244 m, 1210 w, 1180 m, 1140 w, 1067 s, 1009 m, 941 m, 927 w, 880 w, 821 m, 808 m, 795 m, 714 m, 695 m, 569 w, 532 w, 482 w.

RESULTS AND DISCUSSION

As is known [5], formation of metal porphyrins in solution is a result of the bimolecular collision of a porphyrin ligand and a solvated salt ($M(Solv)_4Cl_2$). The complexation reaction rate depends on the coordination interaction of the metal cation with the porphyrin nitrogen atoms and the strength of the N–H bonds of the porphyrin reaction site. The effect of these factors can vary depending on the porphyrin and solvent nature. In the interaction of porphyrin ligands **I**, **III**, and **IV** with $NiCl_2$ in DMF, the transition state energy is dominated by the coordination interaction of the metal cation with the porphyrin nitrogen atoms. Electron-donor aryl substituents in the 5,15-positions of the porphyrin macrocyclic ring enhance the coordination interaction of the solvate complex cation with porphyrin in the transition state. As a result, the formation of Ni^{2+} porphyrinate **VII** is about one order of magnitude faster than that of *meso*-unsubstituted Ni^{2+} porphyrinate **V**. The formation of nickel porphyrinates is about 10 times slower than that of palladium porphyrinates [3]. A similar trend was observed in the complexation reaction of $NiCl_2$ and $PdCl_2$ with tetrabenzoporphine in DMF [6]. Under comparable conditions, Ni^{2+} tetrabenzoporphyrinate forms ~5 times as slow as Pd^{2+} tetrabenzoporphyrinate [6]. This can

Electronic absorption spectra of Ni(II) and Pd(II) porphyrinates in chloroform

Compound	Band I λ, nm (logε)	Band II λ, nm (logε)	Soret band λ, nm (logε)
Ni^{2+}–**I** (**V**)	558 (3.79)	527 (4.11)	412 (5.21)
Ni^{2+}–**II** (**VI**)	552 (4.38)	517 (4.06)	392 (5.19)
Ni^{2+}–**III** (**VII**)		525 (4.10)	418 (5.10)
Ni^{2+}–**IV** (**VIII**)	553 (3.60)	528 (4.31)	414 (5.41)
Pd^{2+}–**I**	555 (3.85)	523 (4.35)	415 (5.43)
Pd^{2+}–**II**	546 (4.69)	513 (4.30)	393 (5.40)
Pd^{2+}–**III**		525 (4.25)	420 (5.40)
Pd^{2+}–**IV**	553 (3.80)	523 (4.50)	415 (5.53)

be evidence that the ionic radius of the $Ni(Solv)_4Cl_2$ solvate complex matches the size of the porphyrin reaction site to a lesser extent than the $Pd(Solv)_4Cl_2$ ionic radius.

The opposite pattern is observed of porphyrazines. The formation rate of Ni^{2+} octaphenyltetraazaporphyrinates is higher than that of Pd^{2+} octaphenyltetraazaporphyrinates [9]. The complexation reaction rate of tetraazaporphyrins with metal salts in strongly coordinating basic solvents is determined by the strength of the N–H bonds of the reaction site [8]. Electron-donor substituents in the porphyrazine molecule enhance the polarization of the N–H bonds and, thus, promote its coordination to $NiCl_2$ in DMF. Under comparable conditions, Ni^{2+} octaphenylporphyrinate is formed in DMF upon heating under reflux for 1 min, whereas Ni^{2+} octa(4-nitrophenyl)tetraazaprophyrinate is formed at room temperature in 20 min [7]. The nitrogen *meso*-atoms in tetraazaporphyrins have electron-withdrawing properties; therefore, Ni^{2+} 5,15-diazaporphyrinate **VI** is formed about a order of magnitude faster than *meso*-unsubstituted Ni^{2+} porphyrinate **V**.

Compounds **V**–**VIII** were identified by elemental analysis, UV and IR spectroscopy, and ^{1}H NMR. Going from nickel porphyrinates to palladium porphyrinates is accompanied by a hypsochromic shift of absorption bands I and II in the UV spectrum (a spectral criterion of strength indicating the strengthening of the $M \leftarrow N$ σ bond and $M \rightarrow N$ π donation) [9]. However, the Soret bands of palladium porphyrinates are bathochromically shifted by 1–3 nm as compared with corresponding nickel porphyrinates **V**–**VIII** (table). Previously [10], anomalous spectral properties have been observed for Ni^{2+} tetrabenzoporphyrinate in a mixed sulfuric acid–dimethyl sulfoxide solvent. The substitution of nitrogen atoms for two *meso*-carbon atoms leads to the hypsochromic shift of the bands in the UV spectrum of nickel porphyrinates (compounds **V** and **VI**). The introduction of bromine atoms in the *para* positions of the phenyl rings (compounds **VII** and **VIII**) leads to a bathochromic shift of band II and to the appearance of band I at 553 nm (table). The change in the geometry of the porphyrin molecule upon complexation with Ni^{2+} ions is clearly manifested in IR spectra: the number of bands decreases because of the degeneracy of odd in-plane vibrations. As compared with octaalkylporphyrin **I** [11], in the IR spectra of Ni^{2+} porphyrinates **V**–**VIII**, the bands of N–H stretching and bending vibrations at 3320 and 965 and 685 cm^{-1} disappear, and strong "metal-sensitive" bands at 1004–1024 cm^{-1} appear. In the ^{1}H NMR spectra, the substitution of nitrogen atoms for two *meso*-carbon atoms (compounds **V** and **VI**) leads to a downfield displacement of the signals of methyl and butyl groups. The aryl and bromoaryl substituents in the 5,15-positions (compounds **VII** and **VIII**) leads to an upfield shift of the signals of C_4H_9 substituents as compared with unsubstituted Ni^{2+} porphyrinate **V**.

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