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Synthesis and Spectral Properties of Bisaxially Coordinated (Octaphenyltetraazaporphyrinato)ruthenium(II) Complexes

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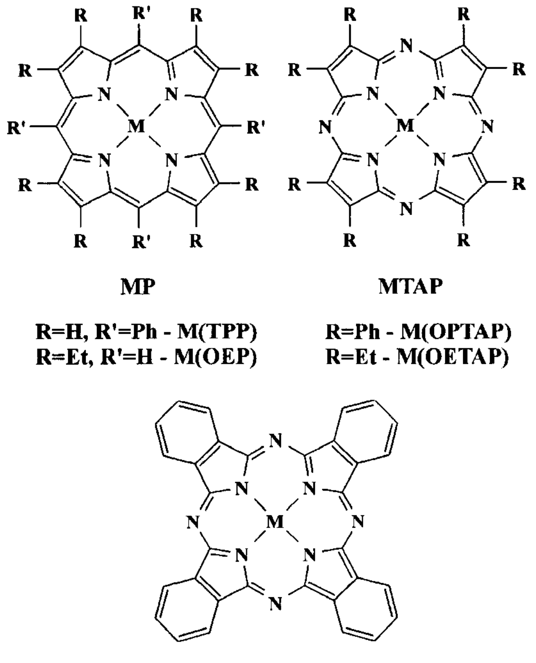
The synthesis of novel bisaxially coordinated ruthenium(II) complexes of octaphenyltetraazaporphine (L_2Ru(OPTAP); L = NH_3, pyridine (py), pyrazine (pyz), *s*-tetrazine (tz), *tert*-butyl isocyanide (*t*-BuNC), and *p*-diisocyanodurole (did)) is reported. Template condensation of diphenylfumaronitrile with pentaammine(dinitrogen)ruthenium(II) dichloride gives the crude compound "Ru(OPTAP)" containing mainly the bis(ammine) derivative $(NH_3)_2$Ru(OPTAP). Heating of "Ru(OPTAP)" with excess of L (L = py, pyz, tz, *t*-BuNC, did) gives L_2Ru(OPTAP) which are readily soluble in organic solvents and can be purified chromatographically. In the case of the bidentate ligands (L = pyz, tz, did) refluxing of the solutions of monomers L_2Ru(OPTAP) results in formation of oligomers with the bridged μ-L coordination. For L = pyz and tz, the sparingly soluble oligomers contain predominantly dimers [(L){Ru(OPTAP)}(μ-L){Ru(OPTAP)}(L)], and, for L = did, the insoluble μ-bridged polymer $[(did)\{Ru(OPTAP)\}((\mu\text{-}did)\{Ru(OPTAP)\})_{x>10}(did)]$ is formed. UV−visible, IR, and ^{1}H NMR spectroscopy and mass spectrometry were used for characterization of the obtained compounds. Cyclic voltammetry study has shown one reduction ($OPTAP^{2-}/OPTAP^{3-}$) and one oxidation (Ru^{II}/Ru^{III}) process (for $(py)_2$Ru(OPTAP) observed at −1.15 and 0.68 V, respectively). Comparison with the data on the corresponding phthalocyanine complexes (L_2Ru(Pc)) reveals the stronger π-back-bonding properties, the higher oxidation potential, and lower aromaticity of the porphyrazine macrocycle present in L_2Ru(OPTAP). These factors along with the lesser extent of oligomerization are responsible for the lower electrical conductivity ($\sigma_{RT} < 10^{-11}$ S/cm) of the μ-bridged Ru(OPTAP) complexes as compared with that of the μ-bridged RuPc polymers.

Introduction

Transition metal complexes of aryl-, and alkyl-substituted tetraazaporphyrins (MTAPs) have become recently an object of intensive studies.[1−3] This is surely connected with the close structural and electronic resemblance of tetraazaporphyrins with phthalocyanines (MPcs) and common porphyrins (MPs) (Chart 1).

MTAPs contain the same stable porphyrazine macrocycle as MPcs, which in the absence of the annulated benzene rings should be less rigid and hence more flexible to deformations.

Chart 1



R=H, R'=Ph - M(TPP)
R=Et, R'=H - M(OEP)

R=Ph - M(OPTAP)
R=Et - M(OETAP)

One can expect that MTAPs combine useful properties of MPcs and MPs. Iron complexes of substituted tetraazaporphyrins have shown catalytic activity in the decomposition of hydrogen

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peroxide (octaphenyl derivative)[4] and in the oxidation of cyclohexane (tetra-*tert*-butyl derivative)[5] which is comparable or higher than that found for FePc. Coordination chemistry, structure, and spectral properties of iron complexes of TAPs have been investigated most comprehensively.[1,2a,d] As for the Fe analogues—complexes of Ru and Os—only a brief note on the octaethyltetraazaporphyrin dimers [M(OETAP)]$_2$ with a metal−metal bond[2b] and some spectral data on bis(pyridine)-octaphenyltetraazaporphyrinates (py)$_2$M(OPTAP)[3] have been published to date.

We report here on the synthesis and spectral properties of bisaxially coordinated ruthenium(II) complexes of octaphenyltetraazaporphine (L$_2$Ru(OPTAP); L = NH$_3$, pyridine (py), pyrazine (pyz), *s*-tetrazine (tz), *tert*-butyl isocyanide (*t*-BuNC), and *p*-diisocyanodurole (did)). For L = pyz, tz, and did, the preparations of compounds with the bridged μ-L coordination of these bidentate ligands have been also attempted. The "shish-kebab" polymers built from phthalocyanine and naphthalocyanine complexes ([(μ-L)M(Pc)]$_n$ and [(μ-L)M(Nc)]$_n$) were shown to be good organic semiconductors.[6] Investigation of the electrical conductivity of the corresponding MTAP polymers [(μ-L)M(TAP)]$_n$ can clarify the influence of the extension of the π-system of the porphyrazine macrocycle on the semiconducting properties of such bridged polymers.

Experimental Section

Diphenylfumaronitrile (DPFN) was prepared from benzyl cyanide according to the literature procedure[7] and purified by vacuum distillation. Preparation of pentaammine(dinitrogen)ruthenium(II) dichloride ([Ru(NH$_3$)$_5$(N$_2$)]Cl$_2$) from RuCl$_3$·3H$_2$O was accomplishedly following the known procedure.[8] Solvents (methanol, CH$_2$Cl$_2$, CHCl$_3$, 1,1,2-trichloroethane), pyridine, pyrazine, and *tert*-butyl isocyanide were pure chemicals (Fluka, Aldrich). *s*-Tetrazine (tz) and *p*-diisocyanodurole (did) were prepared according to the methods given in the literature.[9,10]

Crude "Ru(OPTAP)" was prepared by modification of the method reported elsewere.[3] A well-powdered mixture of DPFN (1.15 g, 5.0 mmol) and [Ru(NH$_3$)$_5$(N$_2$)]Cl$_2$ (0.285 g, 1.0 mmol) was heated to 270 °C and maintained at this temperature until complete solidification (about 30 min). The reaction mixture was powdered, and organic impurities were extracted successively with methanol and dichloromethane. For further purification the product was dissolved in 96% H$_2$SO$_4$, filtered, and promptly precipitated by pouring on ice. After thorough washing with water and drying in a vacuum-desiccator 0.7 g of crude "Ru(OPTAP)" was obtained (yield about 70%, calculated on the amount of [Ru(NH$_3$)$_5$(N$_2$)]Cl$_2$ used).

(NH$_3$)$_2$Ru(OPTAP). Crude "Ru(OPTAP)" was chromatographed on silica gel (eluent tetrahydrofuran), solvent was removed, and the resulting solid was dried in a vacuum. UV−visible (CH$_2$Cl$_2$): λ_{max} = 268 sh, 306, 348, 513, 549, 599 nm. IR (KBr): ν = 3341 w, 3250 w, 3173 w (ν(NH$_3$)), 1601 s (δ_a(HNH)), 1273 m (δ_s(HNH)), 740 m cm^{-1} (ρ_r(NH$_3$)). ^{1}H NMR (D$_2$SO$_4$): δ = 8.45 (m, 40H), −4.7 (s, 6H). Anal. Calcd for the formula (NH$_3$)$_2$Ru(OPTAP), C$_{64}$H$_{46}$N$_{10}$Ru: C, 72.78; H, 4.39; N, 13.26. Found: C, 73.02; H, 4.15; N, 12.87.

(py)$_2$Ru(OPTAP). Crude "Ru(OPTAP)" (60 mg, ∼0.06 mmol) was refluxed 24 h with stirring in 10 mL of pyridine. The reaction mixture was poured in 100 mL of CH$_2$Cl$_2$ and stirred for another 24 h. After filtration the solvents were eliminated and the residue was purified by chromatography (silica gel, CH$_2$Cl$_2$). After removal of the solvent the reddish-brown solid material was dried under vacuum (40 mg, 0.034 mmol, yield ∼60%). UV−visible (CH$_2$Cl$_2$): λ_{max} = 288 nm (log ϵ = 4.79), 342 sh, 349 (4.86), 407 (4.21), 455 sh, 473 (4.41), 541 (4.49), 588 nm (4.98). ^{1}H NMR (CDCl$_3$): δ = 8.25 (m, 16H), 7.50 (m, 16H), 7.41 (m, 8H), 6.30 (m, 2H), 5.56 (m, 4H), 3.04 (m, 4H). FAB-MS (*m/z*): 1180, [M$^+$], 1022 [M$^+$ − 2py]. FD-MS (*m/z*): 1022 [M$^+$ − 2py], 2044 [(M − 2py)$_2{}^+$]. Anal. Calcd for the formula (py)$_2$Ru(OPTAP), C$_{74}$H$_{50}$N$_{10}$Ru: C, 75.30; H, 4.27; N, 11.87. Found: C, 75.18; H, 4.45; N, 11.54%.

(pyz)$_2$Ru(OPTAP). A stirred mixture of crude "Ru(OPTAP)" (300 mg, ∼0.3 mmol) and pyrazine (3 g, 37.5 mmol) was maintained at 100 °C in a sealed vessel. The excess of pyrazine was sublimed off, and the residue was purified by chromatography (silica gel; eluent CH$_2$Cl$_2$). After removal of the solvent the red-brown solid material was dried under vacuum (150 mg, 0.13 mmol, yield ∼ 42%). UV−visible: λ_{max}(CH$_2$Cl$_2$) = 284, 340 sh, 348, 443 sh, 458, 507 sh, 540, 586 nm; λ_{max}(uvasole) = 292, 345 sh, 362, 450 sh, 472, 507 sh, 545, 598 nm. ^{1}H NMR (CDCl$_3$): δ = 8.27 (m, 16H), 7.53 (m, 16H), 7.45 (m, 8H), 6.76 (m, 4H), 2.80 (m, 4H). Anal. Calcd for the formula (pyz)$_2$Ru(OPTAP), C$_{72}$H$_{48}$N$_{12}$Ru: C, 73.08; H, 4.09; N, 14.21. Found: C, 72.93; H, 4.22; N, 14.06.

Oligomers [(pyz){Ru(OPTAP)}((μ-pyz){Ru(OPTAP)})$_x$(pyz)], *x* ≈ 1.25. A saturated solution of (pyz)$_2$Ru(OPTAP) in CHCl$_3$, was refluxed for 5 days under nitrogen. Precipitated insoluble product was separated by filtration, washed with CHCl$_3$, and dried in a vacuum (yield ∼ 20%). The product contains at least 65% of the dimer [(pyz){Ru(OPTAP)}(μ-pyz){Ru(OPTAP)}(pyz)] and less than 35% of higher oligomers *x* ≥ 2. UV−visible (uvasole): λ_{max} = 292, 349 sh, 361, 462, 547 sh, 599 nm. Anal. Calcd for the formula [(pyz){Ru(OPTAP)}(μ-pyz){Ru(OPTAP)}(pyz)], C$_{140}$H$_{92}$N$_{22}$Ru$_2$: C, 73.54; H, 4.06; N, 13.48. Found: C, 72.85; H, 3.85; N, 12.70%.

(tz)$_2$Ru(OPTAP) and [(tz){Ru(OPTAP)}(μ-tz){Ru(OPTAP)}(tz)]. A mixture of crude "Ru(OPTAP)" (200 mg, ∼0.2 mmol) and *s*-tetrazine (350 mg, 4.3 mmol) was refluxed 20 h in 150 mL of 1,1,2-trichloroethane. After the solution was cooled and filtered, the solvent was removed under vacuum at RT (room temperature). Chromatography on silica gel (eluent CH$_2$Cl$_2$) gave several fractions from which the first one contained predominantly the monomer (tz)$_2$Ru(OPTAP) (20 mg, 0.013 mmol, yield ∼ 8%) and the last one the dimer [(tz){Ru(OPTAP)}(μ-tz){Ru(OPTAP)}(tz)] (50 mg, 0.022 mmol, yield ∼ 22%). Anal. Calcd for (tz)$_2$Ru(OPTAP), C$_{68}$H$_{44}$N$_{16}$Ru: C, 68.85; H, 3.74; N, 18.89. Found: C, 69.42; H, 3.86; N, 18.71. UV−visible (CH$_2$Cl$_2$): λ_{max} = 277, 350, 423, 544 sh, 581, 727 sh, 788 sh nm. ^{1}H NMR (CDCl$_3$): δ = 8.30 (m, 16H), 7.59−7.46 (m, 24H), 7.92 (d, 2H), 3.84 (d, 2H) (additional minor peaks of the dimer are also present). Anal. Calcd for [(tz){Ru(OPTAP)}(μ-tz){Ru(OPTAP)}(tz)], C$_{134}$H$_{86}$N$_{28}$Ru$_2$: C, 70.27; H, 3.78; N, 17.12. Found: C, 69.87; H, 3.91; N, 17.53. UV−visible (CH$_2$Cl$_2$): λ_{max} = 270, 345, 419 sh, 544 sh, 582, 684 sh, 747 sh nm. ^{1}H NMR (CDCl$_3$): δ = 8.02 (m, 32H), 7.43−7.34 (m, 48H), 7.68 (d, 2H), 3.26 (d, 2H), 1.80 (s, 2H) (additional minor peaks of the monomer are also present).

(*t*-BuNC)$_2$Ru(OPTAP). Crude "Ru(OPTAP)" (65 mg, ∼0.06 mmol) was suspended in *tert*-butyl isocyanide (1 g, 12 mmol) at 100 °C for 1 day. Then the reaction mixture was chromatographed (silica gel; eluent CH$_2$Cl$_2$) and the blue solid obtained was dried under vacuum (25 mg, 0.21 mmol, yield ∼ 35%). UV−visible (CH$_2$Cl$_2$): λ_{max} = 276 nm (log ϵ = 4.80), 346 sh, 364 (4.97), 421 (4.05), 443 (4.07), 540 (4.47), 585 nm (5.00). IR (KBr): ν = 2135 cm^{-1} vs (ν(NC)). ^{1}H NMR (CDCl$_3$): δ = 8.32 (m, 16H), 7.56−7.42 (m, 24), −0.16 (s, 18H). FD-MS (*m/z*) 1022 [M$^+$ − 2*t*-BuNC], 1105 [M$^+$ − *t*-BuNC], 2044 [(M − 2*t*-BuNC)$_2{}^+$]. Anal. Calcd for the formula (*t*-BuNC)$_2$Ru(OPTAP), C$_{74}$H$_{58}$N$_{10}$Ru: C, 74.72; H, 4.92; N, 11.78. Found: C, 74.58; H, 5.12; N, 11.64.

(did)$_2$Ru(OPTAP) and [(did){Ru(OPTAP)}((μ-did){Ru(OPTAP)})$_x$(did)]. A solution of crude "Ru(OPTAP)" (100 mg, ∼0.1 mmol) and diisocyanodurole (300 mg, 1.6 mmol) in 50 mL of 1,1,2-trichloroethane was refluxed for 30 h. After filtration the solvent was removed under vacuum at RT. The chromatography of the residue

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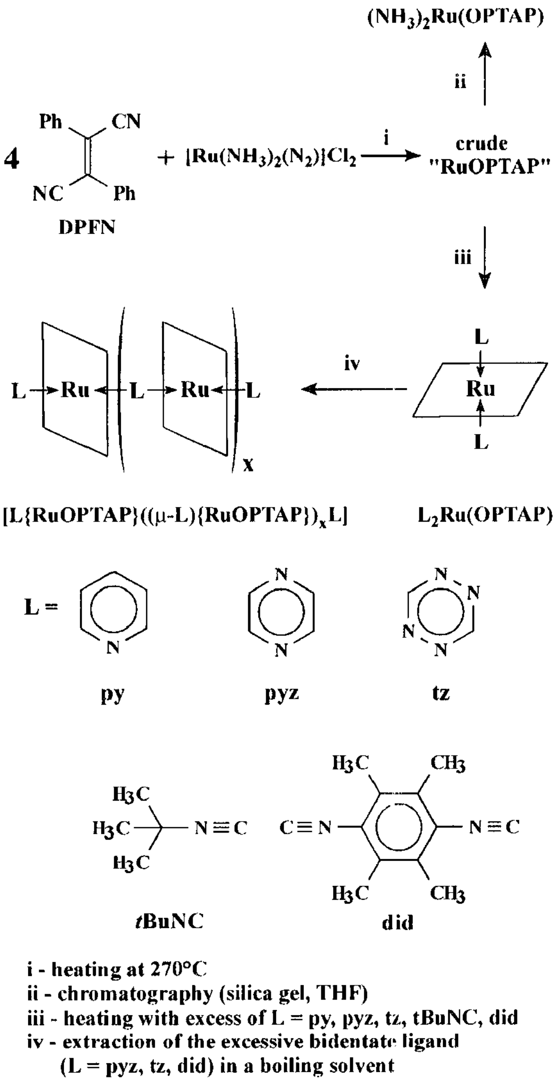
Scheme 1



i - heating at 270°C
ii - chromatography (silica gel, THF)
iii - heating with excess of L = py, pyz, tz, tBuNC, did
iv - extraction of the excessive bidentate ligand
(L = pyz, tz, did) in a boiling solvent

(silica gel; eluent CH_2Cl_2) gave fractions containing monomer $(did)_2Ru(OPTAP)$ with an admixture of soluble oligomers. The monomer is stable only in the presence of excessive did. UV−visible (CH_2Cl_2): λ_{max} = 363, 409 sh, 432 sh, 540 sh, 582 nm. IR (KBr): ν(NC) = 2098−2096 cm^{-1} vs. The solid material obtained after evaporation of CH_2Cl_2 was extracted in a Soxhlet with methanol for 4 days to remove excess of did. The residual insoluble polymer was dried in a vacuum (70 mg, 0.06 mmol, yield ~ 60%). UV−visible (uvasole): λ_{max} = 287, 379, 445, 550 sh, 614 nm. IR (KBr): ν = 2093 cm^{-1} vs (ν-(NC)). Anal. Calcd for the formula [(did){Ru(OPTAP)}((μ-did){Ru(OPTAP)})$_{x>10}$(did)], $(C_{88}H_{64}N_{12}Ru)(C_{76}H_{52}N_{10}Ru)_{x>10}$: C, 75.7; H, 4.4; N, 11.6. Found: C, 76.00; H, 4.35; N, 11.20.

Instrumentation. FT-IR: Bruker IFS 48. UV−visible: Shimadzu UV 2102/3102. NMR: Bruker AC 250 (^{1}H, 250 MHz). MS: Finnigan MAT ISQ 70. Cyclic voltammetry: EG & G PAR-273 potentiostat. Working electrode: Pt disk. Counter electrode: Pt sheet. Reference electrode: Ag wire. Internal reference: ferrocene.

Results and Discussion

Synthesis. Template condensation of $[Ru(NH_3)_5(N_2)]Cl_2$ with diphenylfumaronitrile (DPFN) leads to the formation of the crude "Ru(OPTAP)" (Scheme 1 i). The crude "Ru(OPTAP)" consists mainly of the bis(ammine) derivative $(NH_3)_2Ru(OPTAP)$. Excess of DPFN was removed by washing with methanol and CH_2Cl_2. Complete elimination of unreacted $[Ru(NH_3)_5(N_2)]Cl_2$ from the crude product can be achieved after reprecipitation from 96% H_2SO_4. The IR spectrum shows, along with characteristic bands of the OPTAP macrocycle, the presence of characteristic vibrations of the coordinated NH_3 molecules (see below). The solubility in common organic solvents is too low for ^{1}H NMR study, but the ^{1}H NMR spectra can be obtained in D_2SO_4. The signal for the protons of coordinated NH_3 is observed at very high field at −4.7 ppm. Due to the known tendency of the Ru porphyrin complexes to form dimers with a Ru=Ru bond[2b] we cannot exclude that the crude "Ru(OPTAP)" contains some amount of the dimer $(Ru(OPTAP))_2$. Pure $(NH_3)_2Ru(OPTAP)$ can be obtained by chromatography (silica gel, THF) of the crude "Ru(OPTAP)" (Scheme 1ii). Heating of the crude "Ru(OPTAP)" with large excess of N-bases (L = py, pyz, tz) or isocyanide (L = *t*-BuNC) (with or without solvent) leads to the formation of the bisadducts $L_2Ru(OPTAP)$ (Scheme 1iii). Unreacted $(NH_3)_2Ru(OPTAP)$ is separated by chromatography (silica gel, CH_2Cl_2). In the case of the bidentate ligands (L = pyz, tz, did) monomers $L_2Ru(OPTAP)$ convert easily to the μ-L-bridged oligomers [(L){Ru(OPTAP)}((μ-L){Ru(OPTAP)})$_x$(L)] (Scheme 1iv). Refluxing of a $CHCl_3$ solution of $(pyz)_2Ru(OPTAP)$ gives a mixture of insoluble oligomers, containing predominantly dimer [(pyz){Ru(OPTAP)}(μ-pyz){Ru(OPTAP)}(pyz)] (at least 65%; see below the discussion of IR spectra). The corresponding dimer with tz is more soluble and can be separated from the monomer by chromatography of the reaction mixture. Due to the strong *trans*-effect of isocyanide the monomer $(did)_2Ru(OPTAP)$ is stable in solution only in the presence of excessive did. It cannot be isolated in pure form and in the solid always contains an admixture of some soluble oligomers which cause a variation in the $\nu_{N\equiv C}$ (2098−2096 cm^{-1}) for the samples from different preparations. The continuous extraction of excessive did with boiling methanol gives insoluble polymer [(did){Ru(OPTAP)}((μ-did){Ru(OPTAP)})$_x$(did)] with $x > 10$ (as can be roughly estimated from the elemental analysis data).

Some samples have been characterized by mass spectrometry. In the FAB-MS of $(py)_2Ru(OPTAP)$, M$^+$ (m/z = 1180, 39%) appears along with stronger (M$^+$ − 2py) (m/z = 1022, 94%). No M$^+$ peak was observed in the FD-MS of $(py)_2Ru(OPTAP)$ but only peaks for (M$^+$ − 2py) and dimeric (M − 2py)$_2^+$ (m/z = 2044) ions. The FD-MS of (t-BuNC)$_2$Ru(OPTAP) contains (M$^+$ − 2t-BuNC) (m/z = 1022), (M$^+$ − t-BuNC) (m/z = 1105), and (M − 2t-BuNC)$_2^+$ (m/z = 2044) peaks.

UV−vis spectra have been measured for the CH_2Cl_2 solutions of the monomeric species $L_2Ru(OPTAP)$ (Figure 1) and for the suspensions of the insoluble oligomers in uvasole (Figure 2). The absorption bands in the solid-state spectra are bathochromically shifted as compared to the solution spectra due to the Davydov effect.

The bands of the $\pi \rightarrow \pi^*$ transitions of the OPTAP macrocycle (Q, B, N, L, beginning from the low-energy band) are the most intensive in the spectra. The Q-band which is observed in the visible region (λ_{max} = 580−600 nm) is due to the $1a_{1u} \rightarrow 4e_g^*$ transition. It is typically accompanied by the vibronic satellites on the blue side. The B-band ($3a_{2u} \rightarrow 4e_g^*$ transition) as well as the N- and L-bands appear in the UV region. Comparison of the UV−vis spectra of $L_2Ru(OPTAP)$ and the corresponding complexes of phthalocyanine and 2,3-naphthalocyanine, $L_2Ru(Pc)$ and $L_2Ru(Nc)$ (see Table 1) shows that extension of the conjugated π-system of macrocycle leads to a bathochromic shift of the Q-band and to a hypsochromic shift of the B-band. This is in a good agreement with the theoretical results:[15] annulation of benzene or naphthalene rings to the porphyrazine macrocycle results in the destabilization of

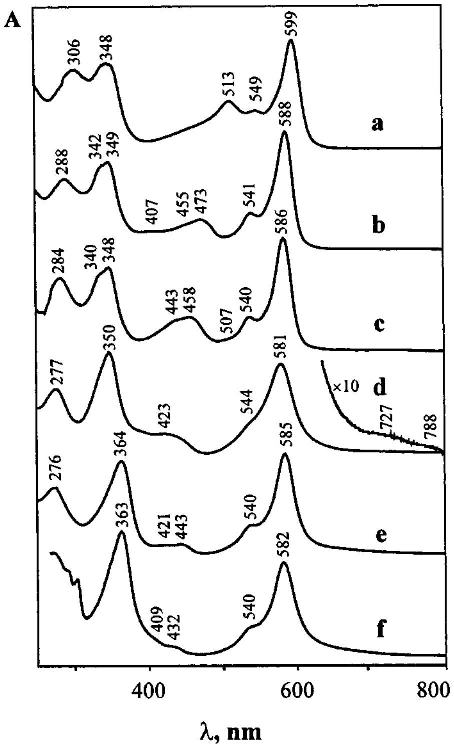


Figure 1. UV−visible spectra of $(NH_3)_2Ru(OPTAP)$ (a), $(py)_2Ru(OPTAP)$ (b), $(pyz)_2Ru(OPTAP)$ (c), $(tz)_2Ru(OPTAP)$ (d), $(t\text{-}BuNC)_2Ru(OPTAP)$ (e), and $(did)_2Ru(OPTAP)$ (in the presence of excessive did) (f) in THF (a) and CH_2Cl_2 (b−f).

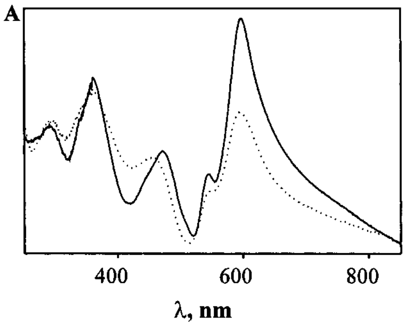


Figure 2. UV−visible spectra of suspensions of the monomer $(pyz)_2Ru(OPTAP)$ (solid line) and oligomer $[(pyz)\{Ru(OPTAP)\}((\mu\text{-}pyz)\{Ru(OPTAP)\})_n(pyz)]$ ($n \approx 1.25$) (dotted line) in uvasole.

π-MO's, which increases in the order $a_{1u} < e_g{}^* < a_{2u}$. This is consistent with $OPTAP^{2-}$ having a higher oxidation potential than Pc^{2-} (see Electrochemistry section below).

For the N-base adducts ($L = NH_3$, py, pyz, tz) the decrease of the σ-donor and increase of the π-acceptor properties of the axial ligand leads to the slight hypsochromic shift of the $\pi \rightarrow \pi^*$ transition bands. The coordinated NH_3 has only σ-donor properties, and the Q, B, and L bands for $(NH_3)_2Ru(OPTAP)$ are shifted to lower energy as compared to the adducts with N-heterocycles (py, pyz, tz) having considerable π-acceptor and weaker σ-donor properties (Table 1). For isocyanides (*t*-BuNC, did) as axial ligands, the Q-band appears at the same position as for py, pyz, or tz, but the B-band is considerably bathochromically shifted. This is evidently connected with the fact that isocyanides are not only strong π-acceptors but also stronger σ-donors than N-heterocycles. As a result, the $3a_{2u}$ orbital, which has significant electron density on the coordinating N-atoms, rises in energy for the isocyanide adducts, and as a consequence, the B-band is shifted to lower energy as compared with the N-base adducts (see Figure 3). The $1a_{1u}$ orbital, having nodes on the internal N-atoms, is less sensitive to the changes on the metal center and remains constant.

The spectral window between Q- and B-bands contains additional bands of lower intensity (Figure 1). For low-spin d^6 complexes of MPcs the absorption bands in this region are usually assigned to the charge transfer (CT) transitions.[11] As was recently shown for bis(pyridine) adducts $(py)_2M(OPTAP)$ (M = Fe, Ru, Os),[1b,3] the strongest of these bands can be connected with the allowed charge transfer (CT) transition M → OPTAP ($d_\pi \rightarrow 2b_{1u}{}^*$) which gains intensity from mixing with $\pi \rightarrow \pi^*$ transitions. The position of this CT band depends strongly on the nature of axial ligands. Only CT M → OPTAP is observed for $(NH_3)_2Ru(OPTAP)$ ($\lambda_{max} = 513$ nm), since coordinated NH_3 has only σ-donor properties. For axial ligands having π-acceptor properties (py < pyz < tz) this CT band (M → OPTAP) undergoes an increasing hypsochromical shift (to 473, 458 and 423 nm, correspondingly) along with strengthening of the π-back-bonding with these ligands and hence lowering of the d_π orbital (Figure 3). Complexation of the second metal atom, acting as a Lewis acid, results in the increase of π-acceptor properties of bridged pyz, and the CT band M → OPTAP is hypsochromically shifted for oligomer $[(pyz)\{Ru(OPTAP)\}((\mu\text{-}pyz)\{Ru(OPTAP)\})_n(pyz)]$ ($n \approx 1.25$) as compared to the monomer $(pyz)_2Ru(OPTAP)$ (from 472 to 460 nm in the solid-state spectra, Figure 2). The position of the M → OPTAP CT band for isocyanide adducts (443 nm for $(t\text{-}BuNC)_2Ru(OPTAP)$ and 432 nm for $(did)_2Ru(OPTAP)$) is indicative of the strong π-acceptor properties of isocyanides.

The assignment of the M → L CT band ($d_\pi \rightarrow (\pi^*)_L$ transition) is less evident. For $[(NH_3)_5RuL]^{2+}$ the CT band Ru → py is observed at 406 nm and Ru → pyz at 472 nm.[16] For the bridged $[(NH_3)_5Ru(\mu\text{-}pyz)Ru(NH_3)_5]^{4+}$ the CT band Ru → pyz is bathochromically shifted to 546 nm.[17] The shoulders at 407 and 507 nm in the spectra of the py and pyz adducts can be ascribed to the M → L CT band. For the tz adduct this CT transition can appear in the long-wavelength region (Figure 1), and for the pyz oligomers the M → μ-pyz CT band is most likely covered under the intensive Q-band envelope (Figure 2). For the isocyanide adducts the M → CNR CT transition is expected in the UV region and may lie under the B-band. Resonance Raman measurements can be helpful in a more reliable assignment of these transitions.

IR spectra of $L_2Ru(OPTAP)$ are typical for complexes of octaphenyltetraazaporphine,[1c,d] and vibration bands of the macrocyclic ligand dominate in the range 600−1800 cm^{-1} (Figure 4, Table S1). Unlike the phenyl ring vibrations, which are stable in their position and intensity, some vibrations of the macrocyclic skeleton are sensitive to the metal and axial ligands. The strong skeleton stretching of the OPTAP macrocycle which is observed about 1487 cm^{-1} for the Fe(II) complexes[1c,d] is shifted to a lower energy of ∼1470 cm^{-1} for the Ru(II) complexes

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Table 1. UV−Vis Spectral Data (λ_{max}, nm (log ϵ)) for Bisaxially Coordinated Ru(II) Complexes of Octaphenyltetraazaporphine, Phthalocyanine, and Naphthalocyanine

	$\pi \rightarrow \pi^*$ transitions					CT and other transitions		
	Q							
compd	(0−0)	(0−1)	B	N	L	L → OPTAP	other	
$(NH_3)_2Ru(OPTAP)$	599	549	348		306	513		
$(py)_2Ru(OPTAP)$	588 (4.98)	541 (4.49)	349 (4.86)	342 sh	288 (4.79)	473 (4.41)	407 (4.21)	455 sh
$(py)_2Ru(Pc)$[11]	626	565	316		284	387		
$(py)_2Ru(Nc)$[12]	717	643	316			429		
$(pyz)_2Ru(OPTAP)$	586	540	348	340sh	284	458	443 sh	507 sh
$(pyz)_2Ru(Pc)$[13]	641	587	314		268	442	376 sh	
$(pyz)_2Ru(Nc)$[12]	721	646	322			416		
$(tz)_2Ru(OPTAP)$	581	544 sh	350		277	423	727 sh	788 sh
$(t\text{-}BuNC)_2Ru(OPTAP)$	585 (5.00)	540 (4.47)	364 (4.97)	346 sh	276 (4.80)	443 (4.07)	421 (4.05)	
$(t\text{-}BuNC)_2Ru(Pc)$[14]	641	582	312			350 sh		
$(t\text{-}BuNC)_2Ru(Nc)$[12]	714	641	325					

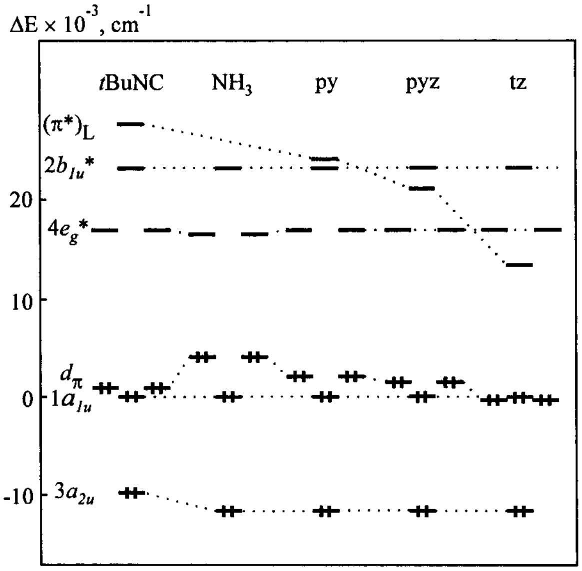

Figure 3. Schematical diagram of the orbitals responsible for the $\pi \rightarrow \pi^*$ and CT transitions in the UV−vis spectra of $L_2Ru(OPTAP)$ (L = t-BuNC, NH_3; py, pyz, tz). The energy of the orbitals are estimated relative to the $1a_{1u}$ orbital on the basis of the experimental UV−vis data.

(Table S1). The position and intensity of the bands at 770, 829, 991, 1005 and 1173 cm^{-1}, which were shown to be sensitive to the oxidation and spin state of the metal atom,[1d] are characteristic for hexacoordinated d^6 complexes. Changes in the axial ligand have a lesser influence on the macrocyclic skeleton vibrations. Increasing of the π-acceptor properties of an axial ligand results in the bathochromic shift of the band about 1170 cm^{-1} (from 1175 to 1165 cm^{-1} for NH_3 and tz adducts, respectively). It is in agreement with the observation that decrease of the M → OPTAP π-back-donation leads to the low-energy shift of this band (from 1166 cm^{-1} for $[(CN)_2Fe(OPTAP)]^{2-}$ to 1152 cm^{-1} for $[(CN)_2Fe(OPTAP)]^{-}$ and 1144 cm^{-1} for (CN)Fe(OPTAP)).[1d] Influence of axial ligands on the position of other skeleton frequencies of the macrocycle do not exceed ±2 cm^{-1}.

Although vibrations of axial ligands are often masked by the stronger vibrations of the macrocycle, their observation gives useful structural information.

In the IR spectrum of the bis(ammine) derivative, $(NH_3)_2Ru(OPTAP)$, the characteristic frequencies of coordinated NH_3 are present as weak-medium bands: NH_3 stretching at 3173, 3250, and 3341 cm^{-1}, NH_3 degenerate deformation at 1601 cm^{-1} (intensifies the weak phenyl ring vibration), NH_3 symmetric deformation at 1273 cm^{-1}, and NH_3 rocking vibrations at 740 cm^{-1}. For the bis(pyridine) adduct, $(py)_2Ru(OPTAP)$, only weak vibrations of coordinated py (1485, 1436, and 1217 cm^{-1}) can be identified in the high-frequency region (Figure 4a).

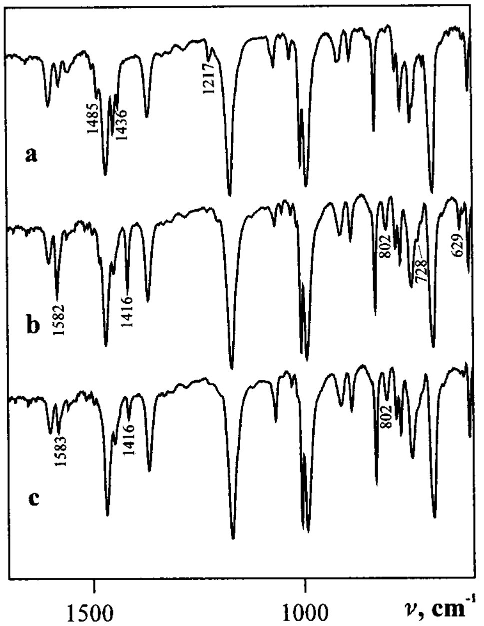

Figure 4. IR spectra of $(py)_2Ru(OPTAP)$ (a), $(pyz)_2Ru(OPTAP)$ (b), and oligomer $[(pyz)\{Ru(OPTAP)\}((\mu\text{-}pyz)\{Ru(OPTAP)\})_n(pyz)]$ ($n \approx 1.25$) (c) in KBr. Listed values indicate characteristic frequencies of the axial ligands.

IR spectroscopy is very helpful in distinguishing the terminal or bridged coordination of the bidentate axial ligands (L = pyz, tz, did) in monomers, $L_2Ru(OPTAP)$, oligomers, $[(L)\{Ru(OPTAP)\}((\mu\text{-}L)\{Ru(OPTAP)\})_x(L)]$, and polymers, $[(\mu\text{-}L)Ru(OPTAP)]_n$, respectively. As was previously shown for the pyz adducts of MPcs,[18] the centrosymmetric pyrazine ring stretching vibration ν_{8a} about 1600 cm^{-1}, which is only Raman-allowed for bidentate pyrazine (D_{2h}) and hence absent in the IR spectra of polymer, becomes IR-allowed in the case of the terminal pyrazine coordination (C_{2v}) and appears in the IR spectra of monomer at 1581 cm^{-1}. The strong band at 1582 cm^{-1} and the medium-strong band at 1416 cm^{-1} are characteristic features of the IR spectrum of $(pyz)_2Ru(OPTAP)$ (Figure 4b). These bands correspond evidently to ν_{8a} (A_g, 1578 cm^{-1}) and ν_{19b} (B_{3u}, 1418 cm^{-1}) fundamentals of pyrazine.[19] The 1582 cm^{-1} band

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Table 2. $\nu_{N\equiv C}$ Stretching Frequencies (cm^{-1}) of Isocyanide Adducts of Ruthenium(II) Complexes with Porphyrazine Type Macrocycles

compd	$\nu_{N\equiv C}$, cm^{-1}	compd	$\nu_{N\equiv C}$, cm^{-1}
free *t*-BuNC	2138	free did	2113
$(t\text{-BuNC})_2Ru(OPTAP)$	2135	$(did)_2Ru(OPTAP)$[a]	~2097
$(t\text{-BuNC})_2Ru(Pc)$[14]	2145	$(did)_2Ru(Pc)$[6b]	2092
$(t\text{-BuNC})_2Ru(Nc)$[12]	2139	$[(\mu\text{-did})Ru(OPTAP)]_n$	2093
$(t\text{-BuNC})_2Ru(TPP)$[20]	2106	$[(\mu\text{-did})Ru(Pc)]_n$[6b]	2084

[a] Contains admixture of oligomers.

becomes IR active due to lowering of the symmetry in unidentate coordinated terminal pyrazine, and its relative intensity band is diminished for the insoluble sample obtained by continuous extraction of excessive pyz (Figure 4c). Comparison of the relative intensities of this ν_{8a} band and the $\gamma_{C=C}$ phenyl absorptions of the OPTAP macrocycle at 692 cm^{-1} for monomer $(pyz)_2Ru(OPTAP)$ ($I(\nu_{8a})/I(\gamma_{C=C}) = 0.371$) and for the insoluble sample ($I(\nu_{8a})/I(\gamma_{C=C}) = 0.164$) gives $n \approx 1.25$ in the general formula of oligomers $[(pyz)\{Ru(OPTAP)\}((\mu\text{-}pyz)\{Ru(OPTAP)\})_n(pyz)]$, which corresponds at least 65% of dimer $[(pyz)\{Ru(OPTAP)\}(\mu\text{-}pyz)\{Ru(OPTAP)\}(pyz)]$ in a mixture of insoluble oligomers. Several other pyz fundamentals can be seen in the IR spectra of the pyz adducts as weak bands. The H-bending ν_{11} (B_{3u}, 804 cm^{-1})[19] appears as a weak band at 802 cm^{-1}. Unlike this band presented in the IR spectra of both species, the bands at 718 and 629 cm^{-1} almost disappear for the dimer and can be counterparted with the Raman-active ν_{10a} (B_{1g}, 757 cm^{-1}) and ν_{6a} (A_g, 596 cm^{-1}) fundamentals of free pyz.[19]

For $(tz)_2Ru(OPTAP)$ several of the tetrazine fundamentals can be observed in the IR spectra. The 1425, 1215, 1119 and 928 cm^{-1} bands might be correlated with the most intense ν_{19b} (B_{3u}, 1448 cm^{-1}), $\nu_{18a,19a}$ (B_{2u}, 1200 cm^{-1}), $\nu_{15,18b}$ (B_{3u}, 1106 cm^{-1}), and $\nu_{11,17b}$ (B_{1u}, 890 cm^{-1}) IR-active fundamentals of free tetrazine.[9] The 1078 cm^{-1} band is probably due to intensification of the weak in-plane deformation mode ν_{12} (B_{2u}, 1090 cm^{-1}). Raman-active fundamentals of free tetrazine (ν_{8b} (B_{1g}, ~1500 cm^{-1}), ν_{6a} (A_g, 737 cm^{-1}), and ν_{6b} (B_{1g}, ~675 cm^{-1})) due to reducing of symmetry from D_{2h} to C_s in unidentate coordinated tetrazine become IR active and appear at 1497, 730, and 653 cm^{-1}, respectively. For the bridged coordinated tetrazine (C_{2h}) these modes are only Raman-allowed and hence their intensity should be lower for oligomers. Comparison of the relative intensities of the 1497 and 692 cm^{-1} bands is suggestive of mainly dimeric structure $[(tz)\{Ru(OPTAP)\}(\mu\text{-}tz)\{Ru(OPTAP)\}(tz)]$ of the compound which was separated chromatographically from the monomer $(tz)_2Ru(OPTAP)$ (($I(\nu_{8b})/I(\gamma_{C=C}) = 0.240$ and 0.472, respectively). The position of the tetrazine vibrations for the dimer differs only slightly from the values of the monomer, and only the ν_{12} in-plane deformation shifts to higher energy by 12 cm^{-1}.

The position of the very strong $\nu_{N\equiv C}$ stretching in the isocyanide adducts is informative about the relationship of the σ-bonding and π-back-bonding effects of coordination. Increasing of σ-bonding tends to raise $\nu_{N\equiv C}$, while strengthening of π-back-bonding should decrease $\nu_{N\equiv C}$. For both alkyl and aryl isocyanide adducts, $(t\text{-BuNC})_2Ru(OPTAP)$ and $(did)_2Ru(OPTAP)$, the $\nu_{N\equiv C}$ value is lower than for free isocyanide (Table 2). The larger shift observed for the did adduct (16 cm^{-1}) as compared with the *t*-BuNC adduct (3 cm^{-1}) indicates that the effect of π-back-bonding prevails over σ-donation in the case of the did coordination. Strengthening of π-back-bonding for aromatic isocyanide adducts was previously observed for other macrocyclic complexes.[14] It is interesting to note that although the molecule of $(did)_2Ru(OPTAP)$ has two types of the $-N\equiv C$ groups (coordinated and noncoordinated), its spectrum contains only the single $\nu_{N\equiv C}$ band, which is indicative about strong charge delocalization. Two did adducts, the soluble monomer $(did)_2Ru(OPTAP)$ and insoluble polymer $[(did)\{Ru(OPTAP)\}((\mu\text{-did})\{Ru(OPTAP)\})_{x>10}(did)]$ (can be abbreviated as $[(\mu\text{-did})Ru(OPTAP)]_n$), have almost identical IR spectra, which differ only in position of the $\nu_{N\equiv C}$ stretching vibration (~2097 and 2093 cm^{-1}, respectively). The lower $\nu_{N\equiv C}$ value for polymer reflects stronger π-back-bonding in the case of bridged did. As can be seen from Table 2 the $\nu_{N\equiv C}$ value for $[(\mu\text{-did})Ru(OPTAP)]_n$ is by 9 cm^{-1} higher than for corresponding phthalocyanine polymer $[(\mu\text{-did})Ru(Pc)]_n$.[6b] This is in agreement with stronger π-acceptor properties of $OPTAP^{2-}$ as compared to Pc^{2-} resulting in strengthening of π-back-bonding with the macrocyclic ligand and its weakening with an axial ligand. For the adduct with an aliphatic isocyanide, $(t\text{-BuNC})_2Ru(OPTAP)$, the $N\equiv C$ stretch is, however, lower than for corresponding phthalocyanine or naphthalocyanine derivatives, $(t\text{-BuNC})_2Ru(Pc)$ and $(t\text{-BuNC})_2RuNc$. Taking into account that π-back-bonding is less significant in binding of aliphatic isocyanides,[14] this points out a weaker σ-bonding of *t*-BuNC by Ru(OPTAP) as compared to RuPc or RuNc. This can be explained by stronger σ-donor properties of $OPTAP^{2-}$ resulting in a higher population of the $4d_{z^2}$ orbital and hence its poorer ability to σ-bind axial ligands. It is interesting to note that the $\nu_{N\equiv C}$ value for $(t\text{-BuNC})_2Ru(OPTAP)$ is by 29 cm^{-1} higher than for $(t\text{-BuNC})_2Ru(TPP)$ (see Table 2), thus indicating much stronger π-acceptor properties of the porphyrazine macrocycle as compared to the porphyrin macrocycle.

^1H NMR spectra give additional information about the structure of obtained compounds. The ^1H NMR data for monomers $L_2Ru(OPTAP)$ (L = py, pyz, tz, *t*-BuNC) are presented in Table 3. In accordance with the low-spin d^6 configuration of the central atom all protons give sharp signals without any broadening or paramagnetic shift. Axial ligands have only a slight influence on the position of the phenyl proton resonances (~8.3, ~7.5, ~7.4 ppm, for *o*-, *m*-, and *p*-protons, respectively). Due to the strong π-electron ring current of the macrocycle, the signals of protons of axial ligands are significantly upfield shifted in comparison to the free ligands. This upfield shift is lesser than that observed for corresponding phthalocyanine complexes (see Table 3). This agrees with the increase of aromaticity of porphyrazine macrocycle due to annulation of benzene rings.[22] In the case of bidentate ligands (L = pyz, tz) the ^1H NMR spectra contain, along with strong multiplets of the Ph protons of monomers $L_2Ru(OPTAP)$, the minor upfield shifted Ph multiplets belonging to the dimer $[(L)\{Ru(OPTAP)\}(\mu\text{-}L)\{Ru(OPTAP)\}(L)]$ (see Figure 5). The most pronounced upfield shift is observed for the *o*-Ph protons—from ~8.3 to ~8 ppm. Protons of the bridged ligand (μ-pyz, μ-tz) in the dimer should give a singlet at higher field as compared with the H^a signal in the monomer. In the case of the μ-pyz bridge connecting two RuOEP units (OEP = octaethylporphyrinate) the signal appears at about −2 ppm.[23] Due to low solubility of the pyz dimer we were unfortunately unable to identify reliably weak pyz signals. For the more soluble tz

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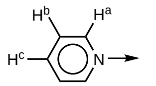
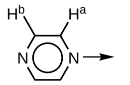
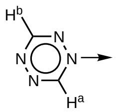
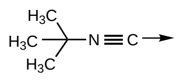
Table 3. ^{1}H NMR Data for L_2Ru(OPTAP) and L_2Ru(Pc) in $CHCl_3$ (δ, ppm)

		chem shifts (δ, ppm)					
		L			OPTAP		
L	compound	H^a	H^b	H^c	*o*-Ph	*m*-Ph	*p*-Ph
	free py $(py)_2$Ru(OPTAP) $(py)_2$Ru(Pc)[21]	8.50 3.04 m 2.43	7.06 5.56 m 5.21	7.46 6.30 m 6.02	 8.25 m	 7.50 m	 7.41 m
	free pyz $(pyz)_2$Ru(OPTAP) $(pyz)_2$Ru(Pc)[13]	8.50 2.80 m 2.35	8.50 6.76 m 6.47		 8.27 m	 7.53 m	 7.45 m
	free tz $(tz)_2$Ru(OPTAP) $(tz)_2$Ru(Pc)[6b]	10.3 3.84 d 3.79 d	10.3 7.92 d 7.69 d		 8.30 m	 7.59−7.46 m	
	free *t*-BuNC (*t*-BuNC)$_2$Ru(OPTAP) (*t*-BuNC)$_2$Ru(Pc)[14]	1.44 −0.16 s −0.49 s			 8.32 m	 7.56−7.42 m	

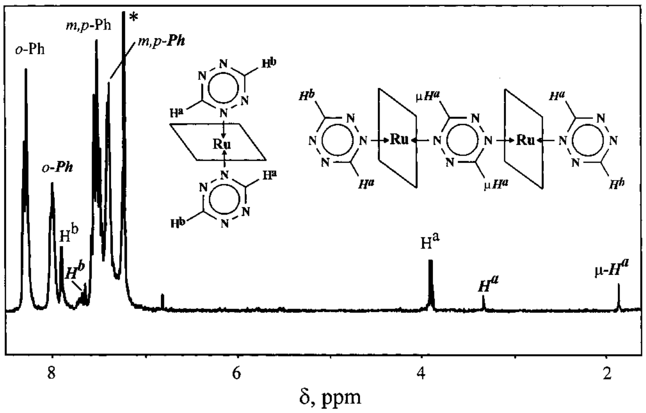


Figure 5. ^{1}H NMR spectrum ($CDCl_3$, 250 MHz) of the tetrazine adducts mixture: monomer $(tz)_2$Ru(OPTAP) and dimer [(tz){Ru-(OPTAP)}(μ-tz){Ru(OPTAP)}(tz)]. Signals of the monomer are marked by normal font, and signals of the dimer, by italics.

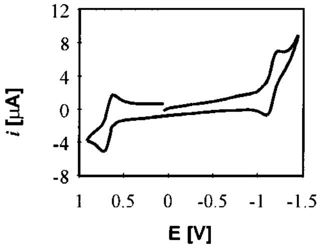


Figure 6. 100 mV/s cyclic voltammogram of $(py)_2$Ru(OPTAP) (~10^{-3} M) in 0.1 M $(n\text{-Bu})_4NPF_6-CH_2Cl_2$ solution.

dimer, [(tz){Ru(OPTAP)}(μ-tz){Ru(OPTAP)}(tz)], the doublets of the terminal coordinated tz and the μ-tz singlet are shifted to the higher field as compared with monomer (by 0.24, 0.58, and 2.04 ppm for *H*^{b}, *H*^{a}, and μ-*H*^{a} protons, respectively).

Electrochemistry of $(py)_2$Ru(OPTAP) and $(pyz)_2$Ru(OPTAP) has been investigated in CH_2Cl_2 using cyclic voltammetry and differential pulse voltammetry. For both compounds two redox processes have been observed—one reduction and one oxidation at −1.15 and 0.68 V for $(py)_2$Ru(OPTAP) (Figure 6) and −0.97 and 0.91 V for $(pyz)_2$Ru(OPTAP). The first oxidation for $(py)_2$Ru(TPP) in CH_2Cl_2 was observed at 0.21 V and ascribed to the Ru^{II}/Ru^{III} couple,[24] whereas for $(py)_2$Ru(Pc) it appears at 0.73 V and occurs on the macrocycle (Pc^{2-}/Pc^- couple).[25] The energy difference between the oxidation and reduction processes (ΔE_{redox} = 1.83 eV) for $(py)_2$Ru(OPTAP) is substantially lower that the energy of the long-wavelength $\pi \rightarrow \pi^*$ transition (Q-band 2.11 eV), thus indicating that the oxidation most probably occurs on the metal (Ru^{II}/Ru^{III}) and not on the macrocycle (OPTAP^{2-}/OPTAP$^-$). For the Cu complex of *tert*-butyl-substituted TAP, Cu(TAP*t*-Bu$_4$), where the macrocycle is the only site of oxidation, ΔE_{redox} = 2.23 eV is close to the energy of the Q-transition (2.13 eV).[26] It must be also noted that even for complexes of TAPs with electron-donating alkyl substituents (Cu(TAP^{t}Bu$_4$), VO(TAP^{t}Bu$_4$),[26] and Mg(OETAP)[27]), the oxidation potential of the tetraazaporphine macrocycle is 0.15−0.45 V higher than for corresponding Pc complexes.[28] As follows from comparison of the acid−base properties of the substituted TAPs, the phenyl substituents unlike the alkyl groups exert an electron-attracting effect on the TAP macrocycle.[29] In view of this it is not surprising that for $(py)_2$Ru(OPTAP) the first oxidation occurs on metal and not on macrocycle. The high potential observed for the (Ru^{II}/Ru^{III}) couple is explained by the stronger π-acceptor properties of the TAP macrocycle present in $(py)_2$Ru(OPTAP) as compared with porphyrin macrocycle in $(py)_2$Ru(TPP). Stronger π-back-bonding abilities of coordinated pyz than that of py stabilize the d_π orbitals of Ru, and the first oxidation potential (0.91 V) is increased for $(pyz)_2$-Ru(OPTAP). The value of ΔE_{redox} = 1.88 V which is lower than the energy of the Q-transition (2.12 eV) implies that in this case oxidation is also localized on Ru. The weaker $d_\pi \rightarrow \pi^*$(OPTAP) interaction in $(pyz)_2$Ru(OPTAP) than in $(py)_2$Ru-(OPTAP) leads to the higher reduction potential of the (OPTAP^{2-}/OPTAP^{3-}) couple (−0.97 and −1.15 V, respectively).

Electrical conductivity (σ_{RT}) of all samples measured by the two-probe technique were lower than 10^{-11} S/cm. Corresponding monomer complexes of phthalocyanine, L_2Ru(Pc),

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have σ_{RT} values of the same order, but for the μ-bridged polymers, $[(\mu\text{-L})Ru(Pc)]_n$, the σ_{RT} values are by several orders of magnitude higher.[6] Low electrical conductivity observed for the μ-bridged Ru(OPTAP) adducts can be explained due to the lesser extent of oligomerization and the higher oxidation potential of the OPTAP macrocycle.

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Supporting Information Available: A table of IR data (1 page). Ordering information is given on any current masthead page.

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