Ordered Supramolecular Porphyrin Arrays from a Building Block Approach Utilizing Pyridylporphyrins and Peripheral Ruthenium Complexes and Identification of a New Type of Mixed-Metal Building Block

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Supramolecular ruthenium complexes (Ru−PyPs) with 4-pyridyl/phenyl porphyrins (PyPs) have been designed and characterized spectroscopically. Ruthenium−dimethyl sulfoxide (Me_2SO) complexes and their carbonyl derivatives were used as precursors to synthesize adducts with Ru:PyP ratios of 1:1 and 1:2 (monomers), 2:1 (dimers), and 4:1 (tetramers). For example, treatment of mono-(pyridyl)porphyrin MPyP (5-(4-pyridyl)-10,15,-20-triphenylporphyrin) with *cis,fac*-$RuCl_2(Me_2SO)_3(CO)$ yielded the 1:1 monomer *cis,cis,cis*-$RuCl_2(Me_2SO)_2(CO)$(MPyP), while reaction with *trans*-$RuCl_2(Me_2SO)_4$ or *trans,cis,cis*-$RuCl_2(CO)_2(Me_2SO)_2$ (2:1 ratio) gave the 1:2 monomers *trans,cis,cis*-$RuCl_2(Me_2SO)_2(MPyP)_2$ and *trans,cis,cis*-$RuCl_2(CO)_2(MPyP)_2$, respectively. Synthesis of the dimers, (*cis*-DPyP)[*cis,cis,cis*-$RuCl_2(Me_2SO)_2(CO)]_2$ and (*trans*-DPyP)[*cis,cis,cis*-$RuCl_2(Me_2SO)_2(CO)]_2$, was accomplished by reaction of the bis-(pyridyl)porphyrins, *cis*-DPyP (5,10-bis(4-pyridyl)-15,20-diphenylporphyrin) and *trans*-DPyP (5,15-bis(4-pyridyl)-10,20-diphenylporphyrin), respectively, with an excess of *cis,fac*-$RuCl_2(Me_2SO)_3(CO)$. Similarly, treatment of 5,10,15,20-tetrakis(4-pyridyl)porphyrin (TPyP) with an excess of *cis,fac*-$RuCl_2(Me_2SO)_3(CO)$ yielded the symmetric tetramer, (TPyP)[*cis,cis,cis*-$RuCl_2(Me_2SO)_2(CO)]_4$. ^1H NMR spectroscopy proved particularly useful for characterizing the Ru−PyPs. Coordination of Ru to the 4-pyridyl groups affected mainly the resonances of the pyridyl ring(s) of the PyPs, causing downfield shifts (H2,6 signals from 0.3 to 0.9 ppm; H3,5 from 0.03 to 0.18 ppm). The pyrrole proton resonances were particularly informative about the geometry of the porphyrin. Treatment of selected Ru−PyP adducts with an excess of zinc acetate produced the corresponding zinc compounds, Ru−Zn·PyPs, in good yield. Most of the Ru−PyPs and Ru−Zn·PyPs are quite soluble in organic solvents like $CHCl_3$ and very robust in solution, where they remain intact for weeks. ^1H NMR and electronic absorption spectra provided evidence that only the Ru−Zn·PyPs with residual Me_2SO units self-assemble spontaneously in solution. The observations are consistent with a self-assembly mode process occuring between the oxygen atom of a Me_2SO ligand of one molecule and the zinc of another molecule.

Introduction

The design and synthesis of complicated molecular systems, a significant goal of modern chemistry,[1] requires molecular components to achieve higher levels of organization. Metal centers, which are endowed with a fundamental structural and ordering role, have been used for several self-assembling supramolecular adducts.[2] In particular, inorganic complexes can easily provide 90° linkages. This unique capability has been exploited for the construction of molecular-sized boxes[3] such as those based on square-planar or octahedral metal centers and rodlike, essentially rigid, bridging components (e.g. 4,4′-bipyridine).[4] Flexible bridging units can be used to construct more elaborate assemblies, such as three-dimensional cavities[3,5] and two- and three-dimensional polymeric metallomacrocyclic networks.[6]

Supramolecular systems containing porphyrins and metalloporphyrins are particularly attractive because these components can introduce desirable photochemical and redox properties. Large arrays of porphyrins have recently become available with the development of "building block" methodologies.[7] Examples can be found in the supramolecular systems for artificial photosynthesis[8] and light harvesting arrays[9] and in the construction of extended π-systems as organic semiconductors, molecular switches, and third-order nonlinear optical materials.[10−13] Macrocyclic porphyrin oligomers with cavities suitable for selective molecular recognition[14] and homogeneous catalysis[15] are also known. Moreover, macrocyclic arrays have been

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obtained by the self-assembly process of suitable metalloporphyrins bearing a pendant basic site.[14d,16]

The above areas are encompassed by the use of mixed 4-pyridyl/phenyl porphyrins (PyPs) as linkers for metal centers. PyPs can provide connections to as many as four metal centers by coordination of the 4-pyridyl groups; depending on whether these centers lie in another porphyrin or in a coordination compound, very different ordered arrays can be constructed. Moreover, metallopyridylporphyrins (M·PyPs) can self-assemble in solution into oligomeric species.[17]

We recently described a series of oligomers of vertically linked porphyrins with PyPs and Zn·PyPs coordinated to Ru(TPP)(CO)(EtOH),[18] and similar assemblies were reported soon after by Imamura's group.[19] Only a few other examples of porphyrins vertically linked through PyPs are known.[20] Also the possibilities of PyPs as ligands in coordination complexes have been investigated only to a limited extent.[21−24] Moreover, many of the investigations involved species generated mainly either in solution[24] or on an electrode surface.[22] Therefore, isolated complexes of PyPs, with well-defined spectroscopic and structural features, are needed for characterizing and understanding the nature of larger molecular arrays produced in this growing field. Such initial characterizations have been recently reported for MPyP complexes with square planar metals.[25] We are focusing on octahedral Ru−dimethyl sulfoxide (Me_2SO) complexes,[26,27] shown to have a high affinity for N-donor ligands such as PyPs.[28] We describe here the design, synthesis, and spectral characterization of a series of (ruthenium complex)−PyP adducts with the following Ru:PyP ratios: 1:1 and 1:2 (monomers), 2:1 (dimers), and 4:1 (tetramers).

Experimental Section

General Methods. Hydrated $RuCl_3$ was a loan from Johnson Matthey. *cis*- and *trans*-$RuCl_2(Me_2SO)_4$[26] and their carbonyl derivatives[27] were prepared according to the literature procedures. All reagents were analytical grade. UV−vis spectra were obtained on a Jasco V-550 spectrophotometer. Excitation and fluorescence spectra were recorded in $CHCl_3$ on a Hitachi F-4500 instrument; porphyrin concentration was, in all cases, 5×10^{-6} M. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100.5 MHz, respectively, on a JEOL EX400 FT instrument. All spectra were run at room temperature. Proton peak positions are referenced to TMS, and assignments were made with the aid of 2D COSY experiments. A pulse delay of 8 s was applied in ^{13}C NMR spectra to allow for relaxation of carbonyl carbon atoms. Solid-state infrared spectra were obtained as Nujol mulls between CsI windows on a Perkin-Elmer 983G spectrometer. Elemental analyses were performed by Dr. E. Cebulec (Dipartimento Scienze Chimiche, Università di Trieste).

Preparations. Except for TPyP, which was acquired from Aldrich and used as received, 4-pyridyl/phenyl porphyrins[37] were prepared according to the method described by Fleischer and Shachter.[17] Thin-layer chromatography of the crude product showed it to be a mixture of the six possible porphyrin isomers. The TLC was run in 98% chloroform and 2% ethanol, and the R_f values of the isomers were (values from ref 17 are given in parentheses) as follows: TPP, 0.92 (0.88); MPyP, 0.83 (0.60); *trans*-DPyP, 0.68 (0.42); *cis*-DPyP, 0.40 (0.22); TrPyP, 0.19 (0.12). The R_f of TPyP was too small to be measured. The R_f values found here differ from those reported previously[17] using the same solvent system but were consistent in five separate preparations of the crude porphyrins.

The isomers were separated using column chromatography. To purify large amounts of MPyP it was easier to use two columns in series: one large column to remove TPP, which constituted approximately 40% of the initial porphyrin mixture, and then a smaller column to separate the other isomers. When the first column was new, it was often possible to separate large amounts of MPyP directly, but for purification of the other isomers a second column was always necessary.

Column One. The column (6×45 cm) was packed with 60 Å 230−400 mesh silica gel (Merck), loaded with 2 g of crude porphyrin, and eluted with a 98:2 chloroform/ethanol mixture. In a typical run, 1.0 g of TPP and 0.8 g of a mixture of PyPs were recovered.

Column Two. Once the TPP (and sometimes also part of MPyP) had been removed, it was possible to separate the remaining PyPs using a smaller column (5×44 cm), packed and eluted as above. In a typical separation, starting from 0.8 g of crude mixture from column 1, the amounts of each isomer obtained were 0.61 g of MPyP, 0.06 g of *trans*-DPyP, and 0.11 g of *cis*-DPyP. TrPyP was usually not recovered. Sometimes the second column yielded a mixture of *trans*-DPyP, *cis*-DPyP, and TrPyP, which were separated with a third, smaller column (2.5×40 cm), packed as above and eluted with a 97:3 chloroform/ethanol mixture. In a typical separation, starting from 0.4 g of mixture from column 2, 0.12 g of *trans*-DPyP and 0.13 g of *cis*-DPyP were obtained.

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The identifications of the porphyrins were confirmed by comparing their R_f values with those of the crude mixture, elemental analysis (Supporting Information), and ^{1}H NMR spectroscopy.

Synthesis of the Complexes. When feasible, all reactions between PyPs and Ru complexes were first monitored by ^{1}H NMR spectroscopy in $CDCl_3$ solution and then performed on a preparative scale. Unless otherwise stated, reactions were quantitative (according to NMR) and very selective. Typical isolated yields, calculated on the limiting reagent, ranged from 55% to 75%.

Unless otherwise stated below, the complexes were prepared according to the following common procedure. A chloroform solution of the proper PyP (a suspension in the case of TPyP) was treated with a stoichiometric amount (1:1 adducts), with a slight deficiency (2:1 adducts), or with a slight excess (oligomers) of the proper Ru complex. The solution was then allowed to react at ambient temperature. The most appropriate reaction time, ranging from 3 h to 8 d, depended mainly on the nature of the complex and was previously evaluated by ^{1}H NMR experiments. The products precipitated as noncrystalline, purple solids after concentration of the solutions to less than half volume (without heating) and addition of some diethyl ether. The products were collected by filtration, washed with cold acetone and diethyl ether, and vacuum dried. According to elemental analysis the products usually contained either 0.5 or 1 crystallization molecule of $CHCl_3$. Sometimes, when suggested by elemental analysis and ^{1}H NMR spectra, the raw products were recrystallized from $CHCl_3$/diethyl ether in good yields.

Zinc(II) was inserted into the ring of coordinated PyPs by reaction at ambient temperature of a chloroform solution of the Ru−PyP complex with an excess of the zinc acetate dissolved in the minimum amount of dimethyl sulfoxide (less than 2 mL) or methanol (in the case of **5**). Average reaction time was 12 h, and reaction completion was assessed by UV/vis spectroscopy.[29] The product precipitated upon addition of some diethyl ether and was washed thoroughly with methanol (to remove unchanged zinc acetate) and then with diethyl ether and vacuum dried.

Elemental analyses and spectroscopic details (UV−vis and selected IR and ^{13}C and ^{1}H NMR data) of Ru complexes described below are reported in the Supporting Information.

***cis,cis,cis*-RuCl$_2$(Me$_2$*S*O)$_2$(CO)(MPyP) (1).** Reaction time: 8 days. Yield of **1** from 75 mg of MPyP (0.12 mmol) and a stoichiometric amount of *cis,fac*-RuCl$_2$(Me$_2$SO)$_3$(CO) in 10 mL of $CHCl_3$: 69 mg (65%).

***cis,cis,cis*-RuCl$_2$(Me$_2$*S*O)$_2$(CO)(Zn·MPyP) (1Zn).** Yield of **1Zn** from 70 mg of **1** (0.06 mmol) in 15 mL of $CHCl_3$ and a 2-fold excess of Zn(CH$_3$COO)$_2$ in DMSO: 70 mg (89%).

***cis,fac*-RuCl$_2$(Me$_2$*S*O)$_3$(MPyP) (2).** Reaction time: 3 h. Yield from 50 mg of MPyP (0.08 mmol) and a stoichiometric amount of *cis*-RuCl$_2$(Me$_2$SO)$_4$ in 10 mL of $CHCl_3$: 46 mg (58%).

***cis,trans,cis*-RuCl$_2$(Me$_2$*S*O)(MPyP)(CO)$_2$ (3).** A mixture of 328 mg of MPyP (0.48 mmol) and 183.5 mg of *cis,trans,cis*-RuCl$_2$(Me$_2$SO)$_2$(CO)$_2$ (0.48 mmol) dissolved in 20 mL of $CHCl_3$ was allowed to react for 10 days at room temperature. The crude product precipitated from the concentrated solution after addition of methanol and was collected on a filter, washed with cold methanol and diethyl ether, and vacuum dried. Yield: 410 mg. According to TLC and ^{1}H NMR spectra, the crude product contained relevant amounts of *trans,cis,cis*-RuCl$_2$(MPyP)$_2$(CO)$_2$ (see below) and unchanged MPyP. Chromatographic purification on a 4.5 × 60 cm column, packed with 60 Å 230−400 mesh silica gel and eluted with a 97:3 dichloromethane−methanol mixture, yielded pure **3** as the central band: 50 mg (11%).

***trans,cis,cis*-RuCl$_2$(Me$_2$*S*O)$_2$(MPyP)$_2$ (4).** Reaction time: 4 h. Yield of **4** from 19.5 mg of *trans*-RuCl$_2$(Me$_2$SO)$_4$ (0.04 mmol) and a slight excess of MPyP in 10 mL of $CHCl_3$: 40 mg (64%).

***trans,cis,cis*-RuCl$_2$(Me$_2$*S*O)$_2$(Zn·MPyP)$_2$ (4Zn).** Yield of **4Zn** from 70 mg of **4** (0.04 mmol) in 30 mL of $CHCl_3$ and a 2-fold excess of Zn(CH$_3$COO)$_2$ in DMSO: 65 mg (85%).

***trans,cis,cis*-RuCl$_2$(CO)$_2$(MPyP)$_2$ (5).** Reaction time: 3 days. Yield from 57.6 mg of *trans,cis,cis*-RuCl$_2$(CO)$_2$(Me$_2$*S*O)$_2$ (0.15 mmol) and a slight excess of MPyP in 20 mL of $CHCl_3$: 190 mg (85%).

***trans,cis,cis*-RuCl$_2$(CO)$_2$(Zn·MPyP)$_2$ (5Zn).** Yield from 100 mg of **5** (0.067 mmol) in 15 mL of $CHCl_3$ and a 2-fold excess of Zn(CH$_3$COO)$_2$ in methanol: 71 mg (65%).

***trans,cis,cis*-RuCl$_2$(Me$_2$*S*O)(CO)(MPyP)$_2$ (6).** Reaction time: 24 h. Yield of **6** from 47.7 mg of *trans*-RuCl$_2$(Me$_2$SO)$_3$(CO) (0.10 mmol) and a slight excess of MPyP in 20 mL of $CHCl_3$: 130 mg (72%).

(*trans*-DPyP)[*cis,cis,cis*-RuCl$_2$(Me$_2$*S*O)$_2$(CO)]$_2$ (7). Reaction time: 3 days. Yield of **7** from 50 mg of *trans*-DPyP (0.074 mmol) and a slight excess of *cis,fac*-RuCl$_2$(Me$_2$SO)$_3$(CO) in 15 mL of $CHCl_3$: 130 mg (65%).

(*cis*-DPyP)[*cis,cis,cis*-RuCl$_2$(Me$_2$*S*O)$_2$(CO)]$_2$ (8). Reaction time: 3 days. Yield of **8** from 50 mg of *cis*-DPyP (0.074 mmol) and a slight excess of *cis,fac*-RuCl$_2$(Me$_2$SO)$_3$(CO) in 15 mL of $CHCl_3$: 120 mg (60%).

(TPyP)[*cis,cis,cis*-RuCl$_2$(Me$_2$*S*O)$_2$(CO)]$_4$ (9). Reaction time: 4 days. Yield of **9** from 71.6 mg of TPyP (0.12 mmol) partially dissolved in 25 mL of $CHCl_3$ and a slight excess of *cis,fac*-RuCl$_2$(Me$_2$SO)$_3$(CO) (a deep purple clear solution was obtained within 2 h): 200 mg (77%).

(Zn·TPyP)[*cis,cis,cis*-RuCl$_2$(Me$_2$*S*O)$_2$(CO)]$_4$ (9Zn). Yield of **9Zn** from 100 mg of **9** (0.046 mmol) in 20 mL of $CHCl_3$ and a 2-fold excess of Zn(CH$_3$COO)$_2$ in DMSO: 63 mg (65%).

(Co·TPyP)[*cis,cis,cis*-RuCl$_2$(Me$_2$*S*O)$_2$(CO)]$_4$ (9Co). To a 100 mg of **9** (0.046 mmol) dissolved in 15 mL of $CHCl_3$, 23 mg of Co(CH$_3$COO)$_2$ (0.13 mmol) dissolved in the minimum amount of MeOH was added. The solution was heated at reflux for 5 h, i.e. until no further change in its visible spectrum was observed. The product precipitated upon concentration of the solution and addition of a few drops of diethyl ether; it was filtered out, washed with cold methanol and diethyl ether, and vacuum dried. Yield: 60 mg (62%).

(TPyP)[*cis,fac*-RuCl$_2$(CO)$_3$]$_4$ (10). Reaction time: 24 h. Yield of **10** from 167.8 mg of TPyP (0.23 mmol) partially dissolved in 45 mL of $CHCl_3$ and a slight excess of *cis,fac*-RuCl$_2$(CO)$_3$(Me$_2$S*O*) (no clear solution was obtained in this case): 250 mg (65%).

[*n*Bu$_4$N]$_4${(TPyP)[*trans*-RuCl$_4$(Me$_2$*S*O)]$_4$} (11). A 0.6 g sample of [*n*Bu$_4$N][*trans*-RuCl$_4$(Me$_2$SO)$_2$] (0.93 mmol), dissolved in 10 mL of $CHCl_3$, was added to 48.2 mg of TPyP (0.078 mmol) partially dissolved in 10 mL of $CHCl_3$. The mixture was stirred overnight at room temperature and then filtered over fine paper to remove unchanged TPyP. The product precipitated from the concentrated solution (5 mL) after addition of diethyl ether; it was filtered out, washed with cold chloroform and diethyl ether, and vacuum dried at room temperature. Yield: 0.12 g (49%). ^{1}H NMR spectrum (DMSO-d_6): 3.21, 1.62, 1.33, 0.94 ppm (*n*Bu$_4$N$^+$); −12.8 ppm (v br, Me$_2$*S*O); −7.0 (br), −1.9 (br), 4.2 ppm (br) (TPyP).

[*n*Bu$_4$N]$_4${(TPyP)[*trans*-RuCl$_4$(CO)]$_4$} (12). A procedure similar to that for **11**, but using [*n*Bu$_4$N][*trans*-RuCl$_4$(CO)(Me$_2$S*O*)] instead of [*n*Bu$_4$N][*trans*-RuCl$_4$(Me$_2$SO)$_2$], was adopted. TPyP was partially dissolved in a mixture of chloroform (10 mL) and acetone (10 mL) to avoid formation of oil. Yield of **12** from 52.3 mg (0.084 mmol) of TPyP and 0.60 g (1 mmol) of [*n*Bu$_4$N][*trans*-RuCl$_4$(CO)(Me$_2$S*O*)]: 70 mg (30%). (The relatively low yields of **11** and **12** can be attributed to their high solubility in the reaction medium.) ^{1}H NMR spectrum (DMSO-d_6): 3.21, 1.62, 1.33, 0.94 ppm (*n*Bu$_4$N$^+$); −5.0 (br), 6.8 ppm (br) (TPyP).

Results

Pyridylporphyrins. Peak integration together with COSY spectra allowed us to assign unambiguously the pyridyl (H2,6 and H3,5), pyrrole (Hβ), and phenyl resonances (*o*-H, *m*-H, and *p*-H) of each PyP (Table 1). The number of NMR signals for the eight pyrrole protons proved to be particularly important in distinguishing between the *cis* and *trans* isomers of DPyP, since the other resonances are only marginally different. *trans*-DPyP has two vertical planes of symmetry, and two doublets of the same intensity (4H each) were observed. *cis*-DPyP has only one plane of symmetry, and two doublets plus two singlets of the same intensity (2H each) were found. The electronic absorption spectra of PyPs ($CHCl_3$) are characterized by a strong Soret band at about 418 nm and four Q-bands of decreasing intensities between 512 and 645 nm (Supporting Information).

(29) Adler, A. D.; Longo, F. K.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.

Table 1. ^{1}H Chemical Shifts of PyPs in $CDCl_3$ (ppm)

	H2,6 (py)	Hβ^a	H3,5 (py)	*o*-H^b	*m*-H + *p*-H^c	NH
MPyP	9.03 (2, m)	8.89 (2, d), 8.85 (4, s), 8.79 (2, d)	8.17 (2, m)	8.21 (6, m)	7.77 (9, m)	−2.80 (2, s)
trans-DPyP	9.04 (4, m)	8.90 (4, d), 8.80 (4, d)	8.16 (4, m)	8.20 (4, m)	7.78 (6, m)	−2.84 (2, s)
cis-DPyP	9.04 (4, m)	8.90 (2, d), 8.87 (2, s), 8.84 (2, s), 8.80 (2, d)	8.16 (4, m)	8.21 (4, m)	7.78 (6, m)	−2.84 (2, s)
TPyP	9.08 (8, m)	8.87 (8, s)	8.16 (8, m)			−2.91 (2, s)

[a] Pyrrole protons. [b] *Ortho* protons of phenyl rings. [c] *Meta* + *para* protons of phenyl rings.

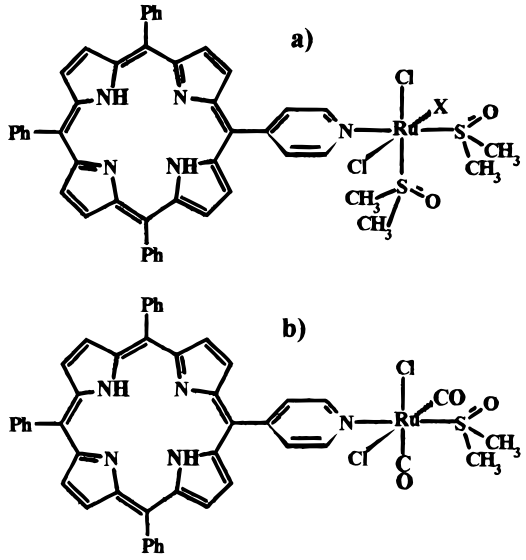

Figure 1. Schematic drawing of the 1:1 Ru−MPyP adducts **1**−**3**: (a) **1**, X = CO, and **2**, X = Me_2SO; (b) **3**.

Their fluorescence spectra, excited at Soret frequencies, show two red-shifted emission peaks (a strong peak at about 647 nm and a much weaker one at about 705 nm) which are the mirror images of their respective absorption bands and are typical of free-base porphyrins.[30] The spectral properties reported in previous work are in general good agreement with our results.[31]

1:1 Ru−MPyP Adducts. MPyP formed 1:1 adducts on treatment with ruthenium complexes that can easily replace one ligand, such as *cis,fac*-$RuCl_2(Me_2SO)_3(CO)$, *cis*-$RuCl_2(Me_2SO)_4$, and *cis,trans,cis*-$RuCl_2(Me_2SO)_2(CO)_2$.

Reaction of MPyP with a stoichiometric amount of *cis,fac*-$RuCl_2(Me_2SO)_3(CO)$ yielded selectively and almost quantitatively *cis,cis,cis*-$RuCl_2(Me_2SO)_2(CO)$(MPyP) (**1**) (Figure 1). The product was unambiguously characterized by combined NMR and IR spectroscopy. The presence of bound CO was assessed by IR and ^{13}C NMR spectroscopy (Supporting Information). The ^{13}C and ^{1}H NMR Me_2SO signals of **1** (Table 2) are consistent with a *cis,cis,cis* geometry for the complex: The expected four ^{13}C NMR signals were found but, due to overlap of two resonances, only three methyl ^{1}H NMR signals in a 2:1:1 ratio were observed. Coordination of Ru induced downfield shifts of the MPyP H2,6 (∼0.5 ppm) and H3,5 (∼0.03 ppm) resonances but almost no shift for the pyrrole and phenyl resonances. Also the UV−vis and fluorescence spectra of MPyP were only marginally affected by coordination to ruthenium. By analogy to the crystallographically characterized *cis,cis,cis*-$RuCl_2(Me_2SO)_2(CO)(py)$,[27b] we propose that in **1** CO is *trans* to Cl and the N-ligand is *trans* to Me_2SO because the ^{13}C NMR signal of the carbonyl carbon in **1** (194.3 ppm) is very close to that found in *cis,cis,cis*-$RuCl_2(Me_2SO)_2(CO)(py)$ (194.0 ppm). Moreover, in the geometrical isomer with the opposite arrangement of ligands, CO would be expected to induce the *trans* Me_2SO ligand to coordinate through oxygen.[27] According to NMR measurements, $CDCl_3$ solutions of **1** did not change appreciably over a period of 4 weeks.

A less robust complex, *cis,fac*-$RuCl_2(Me_2SO)_3$(MPyP) (**2**) (Figure 1), was obtained by reaction between MPyP and *cis*-$RuCl_2(Me_2SO)_4$. The reaction was ∼20 times faster than that with *cis,fac*-$RuCl_2(Me_2SO)_3(CO)$ and involved the replacement by MPyP of the O-bonded Me_2SO in the ruthenium precursor. The product was unambiguously characterized by ^{1}H NMR (Table 2). The pattern of three peaks of equal intensity in the region for S-bonded Me_2SO was that expected for a *fac* geometry. The ^{1}H NMR resonances of MPyP in **2** are similar to those found in **1**. Complex **2** was unstable in chloroform solution and slowly disproportionated to *cis*-$RuCl_2(Me_2SO)_4$ and to two disubstituted isomers formulated as *trans,cis,cis*-$RuCl_2(Me_2SO)_2$(MPyP)$_2$ and, presumably, *cis,cis,cis*-$RuCl_2(Me_2SO)_2$(MPyP)$_2$. While the *trans,cis,cis* complex was easily and selectively obtained by another route (see below), the *cis,cis,cis* isomer was never obtained with a purity higher than 50%: Its ^{1}H NMR spectrum is characterized by four equally intense peaks in the region of S-bonded Me_2SO (4.02, 3.70, 3.40, and 3.32 ppm) and by broad resonances for the two MPyP units. The broadness of aromatic resonances found in the pyridine analog, *cis,cis,cis*-$RuCl_2(Me_2SO)_2(py)_2$, was unambiguously attributed to the relatively slow rotation of the pyridine rings about the Ru−N bond.[32] Such a fluxional process reasonably accounts for the broad signals observed here.

Another stable compound, *cis,trans,cis*-$RuCl_2(Me_2SO)$(MPyP)$(CO)_2$ (**3**) (Figure 1), was obtained by reaction of MPyP with *cis,trans,cis*-$RuCl_2(Me_2SO)_2(CO)_2$. A certain amount of the disubstituted product *trans,cis,cis*-$RuCl_2(CO)_2$(MPyP)$_2$ (see below) formed during the reaction and was eliminated by column chromatography. The geometry of **3** was unambiguously established spectroscopically: two IR CO stretching bands, a single CO ^{13}C NMR resonance, and a single ^{1}H NMR resonance for the two equivalent methyl groups of the nonleaving Me_2SO (Table 2).

1:2 Ru−MPyP Adducts. MPyP and *trans*-$RuCl_2(Me_2SO)_4$ (2:1 ratio) rapidly and selectively formed the disubstituted adduct *trans,cis,cis*-$RuCl_2(Me_2SO)_2$(MPyP)$_2$ (**4**) (Figure 2). The stoichiometry and the geometry of the complex were unambiguously established spectroscopically. The solid-state IR spectrum has a single Ru−Cl stretching band at 342 cm^{-1}, characteristic of mutually *trans* chlorides. The ^{1}H NMR spectrum of **4** (Table 3) reflects the symmetry of the complex, with two equivalent MPyP ligands and two equivalent Me_2SO ligands. Moreover, the *o*-H and the *m*+*p*-H multiplets of MPyP are each separated into two new multiplets (see Discussion). When the formation of **4** was followed by NMR spectroscopy, a 1:1 intermediate (from integration) characterized by a downfield H2,6 (10.00 ppm, downfield compared to **4**) was observed in the first few minutes of reaction. The corresponding resonances of Me_2SO, two singlets at 3.40 and 3.56 ppm in a 2:1 intensity ratio, suggest a *mer* geometry for this 1:1 intermediate.

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(31) (a) Shamim, A.; Worthington, P.; Hambright, P. *J. Chem. Soc. Pak.* **1981**, *3*, 1. (b) Sari, M. A.; Battioni, J. P.; Dupré, D.; Mansuy, D.; Le Pecq, J. B. *Biochemistry* **1990**, *29*, 4205. (c) Meng, G. G.; James, B. R.; Skov, K. A. *Can. J. Chem.* **1994**, *72*, 1894.
(32) Alessio, E.; Calligaris, M.; Roppa, R.; Marzilli, L. G. Unpublished results.

Table 2. Selected ^{1}H Chemical Shifts of 1:1 Ru−MPyP Compounds **1**−**3** in $CDCl_3$ (ppm)

	H2,6 (py)	Hβ^a	H3,5 (py)	*o*-H^b
cis,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)$(MPyP) (**1**)	9.46 (2, m)	8.91 (2, d), 8.85 (6, m)	8.24 (2, m)	8.20 (6, m)
cis,*fac*-$RuCl_2(Me_2SO)_3$(MPyP) (**2**)	9.52 (2, m)	8.89 (2, d), 8.85 (4, m),^{d} 8.77 (2, d)	8.20 (2, m)^c	8.20 (6, m)^c
cis,*trans*,*cis*-$RuCl_2(Me_2SO)$(MPyP)$(CO)_2$ (**3**)	9.29 (2, m)	8.94 (2, d) 8.86 (4, m),^{d} 8.31 (2, d)	8.31 (2, m)	8.21 (6, m)

^{a} Pyrrole protons. ^{b} *Ortho* protons of phenyl rings. ^{c} Overlapping peaks. ^{d} Unresolved multiplet.

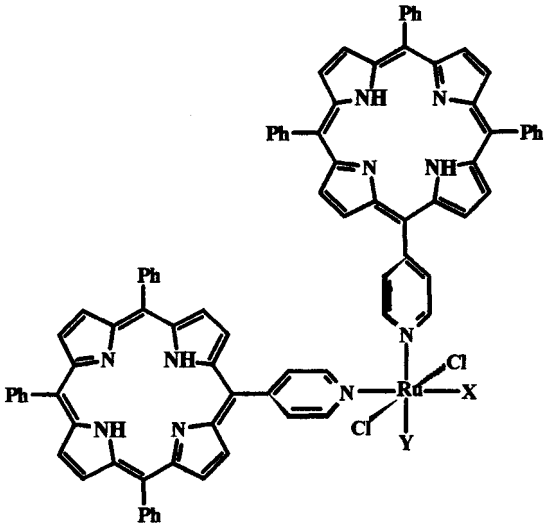

Figure 2. Schematic drawing of the 1:2 Ru−MPyP adducts **4**−**6**: **4**, X = Y = Me_2SO; **5**, X = Y = CO; **6**, X = Me_2SO, Y = CO.

The complex *trans*,*cis*,*cis*-$RuCl_2(CO)_2(MPyP)_2$ (**5**) (Figure 2), similar to **4** but with two CO molecules in place of the Me_2SO ligands, was obtained by reaction of *trans*,*cis*,*cis*-$RuCl_2(CO)_2(Me_2SO)_2$ with 2 equiv of MPyP. Combined IR and ^{13}C NMR evidence confirmed that **5** has two *trans* chlorides and two *cis* CO ligands (Supporting Information). The ^{1}H NMR signals of the two equivalent MPyP units in **5** are similar to those found in **4** (Table 3), even though the resonance of H2,6 is less downfield shifted (0.55 ppm *vs* 0.80 ppm in **4**). A similar difference was found for the H2,6 signals in the pyridine derivatives, *trans*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(py)_2$ (9.14 ppm) and *trans*,*cis*,*cis*-$RuCl_2(CO)_2(py)_2$ (8.89 ppm).[32] The reaction leading to *trans*,*cis*,*cis*-$RuCl_2(CO)_2(MPyP)_2$ was considerably slower compared to that yielding *trans*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(MPyP)_2$ and occurred in two well-separated steps. In fact, the monosubsituted intermediate *trans*,*cis*,*cis*-$RuCl_2(CO)_2(Me_2SO)$(MPyP) built up very rapidly, within minutes after mixing (residual Me_2SO signal at 2.97 ppm), while coordination of the second MPyP moiety to form **5** required several hours. Complex **5** was obtained also as a minor product from the reaction of MPyP with *cis*,*trans*,*cis*-$RuCl_2(Me_2SO)_2(CO)_2$.

Finally, a *cis*-disubstituted complex with nonequivalent MPyP units, *trans*,*cis*,*cis*-$RuCl_2(Me_2SO)(CO)(MPyP)_2$ (**6**) (Figure 2), was obtained by reaction of *trans*-$RuCl_2(Me_2SO)_3(CO)$ with 2 equiv of MPyP. The porphyrin replaced the Me_2SO *trans* to CO and one of the two Me_2SO's *trans* to each other. In **6** the pyridyl signals of the two inequivalent porphyrins are well resolved, whereas the signals of the phenyl rings overlap (Table 3). The H2,6 and H3,5 signals of each porphyrin unit have been related by means of a COSY spectrum. When the above reaction was followed by ^{1}H NMR spectroscopy, two monosubstituted intermediates were observed, one with MPyP *trans* to CO (resonance at 3.46 ppm for the two equivalent Me_2SO ligands) and the other with MPyP *trans* to Me_2SO (equally intense resonances at 2.89 and 3.54 ppm for the residual Me_2SO and Me_2SO, respectively).

The intensities of the electronic absorption and emission spectra of the *cis* disubstituted complexes seem to depend on the number of residual Me_2SO ligands. While the molar absorption coefficient per porphyrin (ϵ/MPyP) of the Soret band of *trans*,*cis*,*cis*-$RuCl_2(CO)_2(MPyP)_2$ is substantially unchanged compared to MPyP, ϵ/MPyP is ∼40% lower for *trans*,*cis*,*cis*-$RuCl_2(CO)(Me_2SO)(MPyP)_2$ and *trans*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(MPyP)_2$. A similar behavior was observed in the emission spectra, where the intensity of the main fluorescence band at 647 nm greatly decreased from *trans*,*cis*,*cis*-$RuCl_2(CO)_2(MPyP)_2$ to *trans*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(MPyP)_2$.

Dimers. The selectivity of the reaction of *cis*,*fac*-$RuCl_2(Me_2SO)_3(CO)$ with MPyP and the stability of the 1:1 adduct *cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)$(MPyP) (**1**) prompted us to consider this precursor as the one most suited for the synthesis of stable compounds of higher nuclearity. *trans*-DPyP selectively added 2 equiv of *cis*,*fac*-$RuCl_2(Me_2SO)_3(CO)$. The ^{1}H NMR spectrum of the dimeric product (*trans*-DPyP)[*cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)]_2$ (**7**) (Figure 3, Table 4) confirmed that the two ruthenium units are equivalent, each bearing two sulfoxides and having the expected *cis*,*cis*,*cis* geometry. The resonances of the two ruthenium units are very similar to those of **1**. For example, as in **1**, the four expected methyl resonances of **7** were well resolved in the ^{13}C NMR spectrum, but two overlapped in the ^{1}H NMR spectrum. The pyrrole resonances (two doublets accounting for 4 protons each) indicate that in **7** the *trans* symmetry of the porphyrin was maintained with the two complexes rotating rapidly enough on the NMR time scale so as not to break the two mirror planes.

Similarly, (*cis*-DPyP)[*cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)]_2$ (**8**) (Figure 4), an isomer of **7**, was obtained by reaction of *cis*-DPyP with 2 equiv of *cis*,*fac*-$RuCl_2(Me_2SO)_3(CO)$. The spectrum of **8** (Table 4) is remarkably similar to that of **7** except for the pyrrole resonances, which consist of two doublets and two singlets (even though coordination to ruthenium induced partial overlap), characteristic of the symmetry of *cis*-DPyP. Since the *cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)$ moiety is chiral, meso (*CA*)[33] and diastereoisomeric (*CC* and *AA*) forms of **7** and **8** undoubtedly exist with potentially different NMR signals. However, at the field used, the ^{1}H and ^{13}C NMR signals were not distinct for the two forms.

Tetramers. Tetramers bearing four equivalent units of either Ru(II) or Ru(III) complexes were easily obtained by reaction of TPyP with an excess of the ruthenium precursor. For example, reaction with *cis*,*fac*-$RuCl_2(Me_2SO)_3(CO)$ selectively yielded (TPyP)[*cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)]_4$ (**9**) (Figure 5). Complex **9** is remarkably more soluble in chloroform than TPyP. Even though **9** must exist as a mixture of stereoisomers (with *C* or *A* Ru units), it has a particularly simple NMR spectrum (Table 4), indicating that all four Ru units have the expected *cis*,*cis*,*cis* geometry. The presence of stereoisomers induces only a slight broadening of the resonances, suggesting that the units are not close enough to have an effect on the shifts.

The tetramer (TPyP)[*cis*,*fac*-$RuCl_2(CO)_3]_4$ (**10**), obtained by reaction with *cis*,*fac*-$RuCl_2(CO)_3(Me_2SO)$, proved instead to be almost insoluble in most organic solvents. Two rather soluble tetraanionic Ru(III) compounds, $[nBu_4N]_4${(TPyP)[*trans*-$RuCl_4(Me_2SO)]_4$} (**11**) and $[nBu_4N]_4${(TPyP)[*trans*-$RuCl_4(CO)]_4$} (**12**)

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Table 3. Selected ^{1}H Chemical Shifts of 1:2 Ru−MPyP Products **4**−**6** (and **5Zn**) in $CDCl_3$ (ppm)

	H2,6 (py)	Hβ[a]	H3,5 (py)	*o*-H (15)[b]	*o*-H (10, 20)[c]	*m*-H + *p*-H (15)[d]	*m*-H + *p*-H (10, 20)[e]
trans,*cis*,*cis*-$RuCl_2(Me_2SO)_2(MPyP)_2$ (**4**)	9.83 (4, m)	8.84 (4, d), 8.80 (4, d), 8.77 (4, d), 8.72 (4, d)	8.30 (4, m)	8.19 (4, m)[f]	8.05 (8, m)[g]	7.76 (6, m)[f]	7.54 (12, m)[g]
trans,*cis*,*cis*-$RuCl_2(CO)_2(MPyP)_2$ (**5**)	9.58 (4, m)	8.85 (16, m)	8.45 (4, m)	8.21 (4, m)[f]	8.15 (8, m)[g]	7.76 (6, m)[f]	7.68 (12, m)[g]
trans,*cis*,*cis*-$RuCl_2(CO)_2(Zn{\cdot}MPyP)_2$ (**5Zn**)	9.57 (4, m)	8.94 (16, m)	8.45 (4, m)	8.20 (4, m)[f]	8.14 (8, m)[g]	7.76 (6, m)[f]	7.67 (12, m)[g]
trans,*cis*,*cis*-$RuCl_2(Me_2SO)(CO)(MPyP)_2$ (**6**)	9.85 (2, m),[f] 9.40 (2, m)[g]	8.84 (16, m)	8.42 (2, m),[f] 8.32 (2, m)[g]	8.19 (4, m)[f]	8.12 (8, m)[g]	7.76 (6, m)[f]	7.64 (12, m)[g]

[a] Pyrrole protons. [b] *Ortho* protons of phenyl ring at position 15. [c] *Ortho* protons of phenyl rings at positions 10 and 20. [d] *Meta* + *para* protons of phenyl ring at position 15. [e] *Meta* + *para* protons of phenyl rings at positions 10 and 20. [f,g] Peaks related to each other in the COSY spectrum.

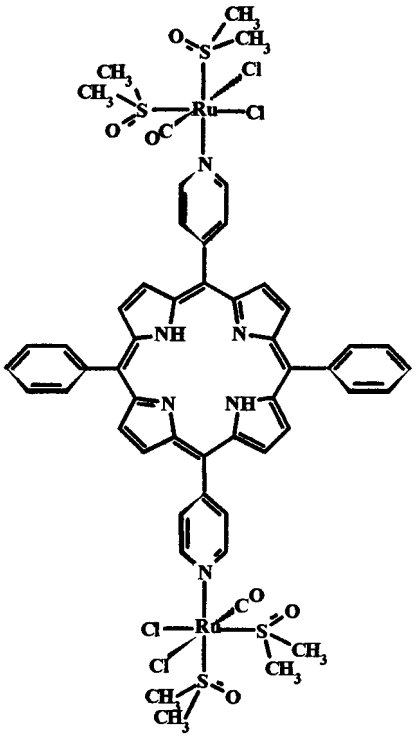

Figure 3. Schematic drawing of (*trans*-DPyP)[*cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)]_2$ (**7**).

(nBu$_4$N = *n*-tetrabutylammonium), were obtained similarly by reaction with [nBu$_4$N][*trans*-$RuCl_4(Me_2SO)_2$] and [nBu$_4$N][*trans*-$RuCl_4(CO)(Me_2SO)$], respectively. The DMSO-d_6 ^{1}H NMR spectrum of **11** has, besides the resonances of the cation, a very broad peak for Me_2SO (−12.8 ppm) and three broad resonances (−7.0, −1.9, and 4.2 ppm) ascribable to TPyP in a symmetric environment. The ^{1}H NMR spectrum of **12** is similar to that of **11**, except for the absence of the Me_2SO resonance and a general downfield shift of the three MPyP signals of about 2 ppm.

Insertion of Metal Ions and Self-Assembly Processes. In principle, two complementary approaches can be pursued for the incorporation of metal ions into the porphyrin unit(s) of the above compounds, i.e. synthesis of metal−PyPs followed by reaction with the Ru precursors or insertion of the metal ion into the isolated Ru−PyP complex. We found the second method was definitely superior; treatment of selected Ru−PyP adducts with an excess of zinc acetate in chloroform/DMSO or chloroform/methanol solution yielded the corresponding zinc compounds in good yield. Similarly, Co^{2+} was inserted into the tetramer (TPyP)[*cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)]_4$ (**9**), leading to good yields of **9Co**. The insertion of metal ions into the porphyrin core led to a general slight decrease in the solubility of the complexes in chloroform (see also below). Insertion of zinc altered the visible absorption spectra of the complexes, i.e. two Q-bands instead of four and a general red shift of the Soret band (5−6 nm); these changes are similar to those found upon metalation of free porphyrins.[30] Insertion changed the general shape of the emission spectra of the complexes, characterized now by a main fluorescence band at about 605 nm, accompanied by a shoulder at about 645 nm (λ_{ex} = 420−430 nm).[20c] Fluorescence intensity was also reduced by ∼15−40% relative to the zinc-free complexes.

We found that in *cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)(MPyP)$ (**1**), *trans*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(MPyP)_2$ (**4**), and (TPyP)[*cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)]_4$ (**9**) insertion of zinc into the PyP core induced a self-assembly process in solution. Experimental evidence came from the following measurements (all in chloroform):

(1) ^{1}H NMR Spectra. As expected, the spectra of *cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)(Zn{\cdot}MPyP)$ (**1Zn**) and *trans*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(Zn{\cdot}MPyP)_2$ (**4Zn**) lacked the NH signals. However, all resonances, particularly those of the Me_2SO and pyridyl protons, were shifted considerably upfield and broadened compared to those of the corresponding precursor. This was remarkably more pronounced in **4Zn** than in **1Zn**. For example, in a 2.5 mM $CDCl_3$ solution of *cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)$-(Zn·MPyP) the two Me_2SO ligands gave four slightly broadened resonances between 2.97 and 2.74 ppm (Figure 6), while in an equimolar solution of *trans*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(Zn{\cdot}MPyP)_2$ the two equivalent Me_2SO ligands gave a very broad signal at 0.7 ppm. Similar evidence for self-assembly was found in the aromatic region. The pyridyl and pyrrole resonances of *trans*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(Zn{\cdot}MPyP)_2$ were broadened and shifted upfield, while the pyridyl resonances only of *cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)(Zn{\cdot}MPyP)$ were affected and to a lesser degree than for **4Zn** (Figure 7). Moreover, the ^{1}H NMR spectra of both compounds were strongly dependent upon temperature and concentration: Both an increase in the temperature and a decrease in the complex concentration induced a general downfield shift and sharpening of all resonances, particularly the Me_2SO and pyridyl H2,6 signals (Figure 6). (Note: The spectral changes with temperature were reversible in the range examined.) Similar results were obtained by addition of a competitive solvent such as CD_3OD: The spectra of both *cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)(Zn{\cdot}MPyP)$ and *trans*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(Zn{\cdot}MPyP)_2$ became very similar to those of *cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)(MPyP)$ and *trans*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(MPyP)_2$, respectively, upon increasing the amount of added CD_3OD (Figure 7). Unlike *cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)(Zn{\cdot}MPyP)$ and *trans*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(Zn{\cdot}MPyP)_2$, the tetramer (Zn·TPyP)[*cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)]_4$ (**9Zn**) was almost insoluble in $CDCl_3$ (solubility ∼10^{-4} M). However, addition of a few microliters of CD_3OD completely dissolved the complex, which then had an ^{1}H NMR spectrum very similar to that of (TPyP)[*cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)]_4$. The dissolution of **9Zn** is consistent with methanol binding to Zn, since

Table 4. Selected ^{1}H Chemical Shifts of Dimers **7** and **8** and Tetramers **9** and **10** in $CDCl_3$ (ppm)

	H2,6 (py)	Hβ^a	H3,5 (py)
(*trans*-DPyP)[*cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)]_2$ (**7**)	9.47 (4, m)	8.92 (4, d), 8.86 (4, d)	8.23 (4, m)
(*cis*-DPyP)[*cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)]_2$ (**8**)	9.49 (4, m)	8.88 (8, m)	8.24 (4, m)
(TPyP)[*cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)]_4$ (**9**)	9.52 (8, m)	8.94 (8, s)	8.22 (8, m)
(TPyP)[*cis*,*fac*-$RuCl_2(CO)_3]_4$ (**10**)^b	9.41 (8, m)	9.03 (8, s)	8.44 (8, m)

^{a} Pyrrole protons. ^{b} CD_2Cl_2 solution.

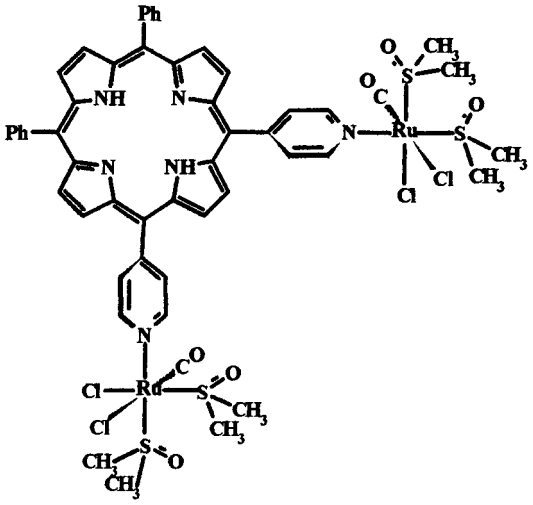

Figure 4. Schematic drawing of (*cis*-DPyP)[*cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)]_2$ (**8**).

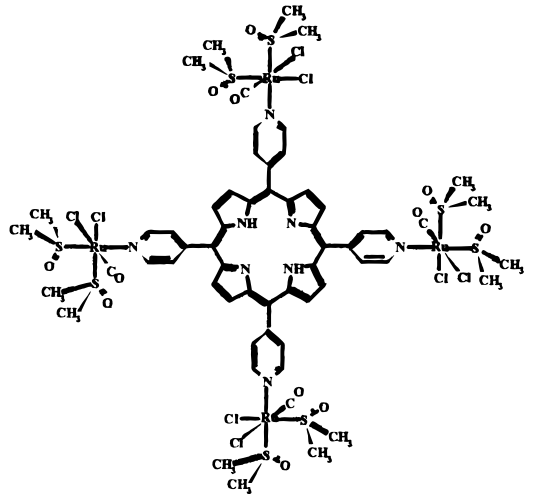

Figure 5. Schematic drawing of (TPyP)[*cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)]_4$ (**9**).

methanol does not dissolve these compounds but can be used, in place of diethyl ether, to precipitate them from chloroform solution.

(2) UV−Vis Absorption Spectra. The molar extinction coefficients (ϵ) of the Soret band of *cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)$(Zn·MPyP), *trans*,*cis*,*cis*-$RuCl_2(Me_2SO)_2$(Zn·MPyP)$_2$, and (Zn·TPyP)[*cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)]_4$ were strongly concentration dependent. In general, ϵ gradually increased with decreasing concentration; the effect was observed at different ranges of concentration. In particular, ϵ of *cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)$(Zn·MPyP) remained constant for concentrations in the range $5 \times 10^{-7}-3 \times 10^{-6}$ M and then decreased by ~60% from 3×10^{-6} to 10^{-5} M (higher concentrations could not be investigated). The ϵ of the disubstituted complex *trans*,*cis*,*cis*-$RuCl_2(Me_2SO)_2$(Zn·MPyP)$_2$ was essentially constant in the range $10^{-7}-2 \times 10^{-6}$ M and then started to decrease, even though concentrations higher than 4×10^{-6} M could not be investigated. For (Zn·TPyP)[*cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)]_4$

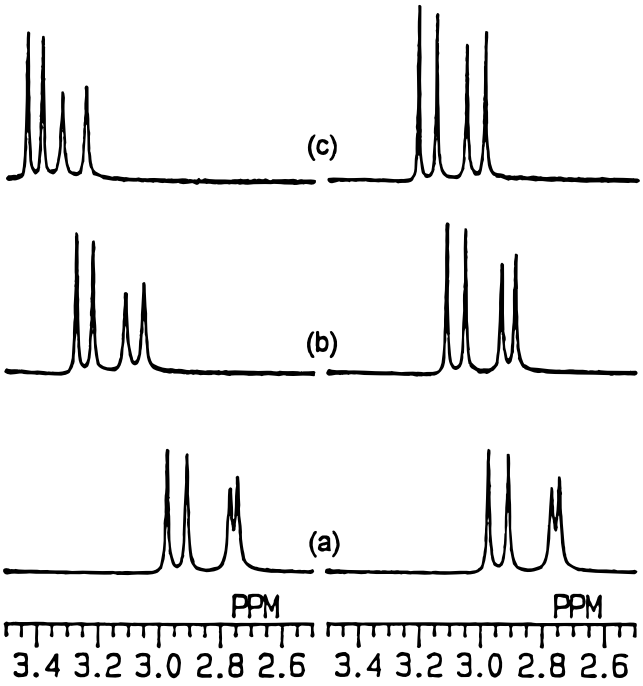

Figure 6. Effect of dilution (left) and temperature (right) on the ^{1}H NMR Me_2SO signals of *cis*,*cis*,*cis*-$RuCl_2(Me_2SO)_2(CO)$(Zn·MPyP) (**1Zn**). Left: $T = 25$ °C; [**1Zn**] = 2.50 mM (a), 1.25 mM (b), 0.62 mM (c). Right: [**1Zn**] = 2.50 mM, $T = 25$ °C (a), 35 °C (b), 45 °C (c).

ϵ was essentially constant from 10^{-5} to 5×10^{-7} M and then steadily increased for lower concentrations. This behavior has been reported previously for self-assembling porphyrin systems.[16] No concentration-dependent shifts in the position of the absorption maxima were observed. Therefore, the hypothetical interaction of Zn with dissociated PyPs, which would involve a bathochromic shift of the Soret band,[16] can be ruled out.

In contrast, *trans*,*cis*,*cis*-$RuCl_2(CO)_2$(Zn·MPyP)$_2$ (**5Zn**), which lacks the Me_2SO ligands, has an ^{1}H NMR spectrum very similar to that of **5** (Table 3) with all sharp resonances.[38] Insertion of Zn^{2+} did not shift the pyridyl signals, but the pyrrole resonances were slightly downfield shifted (0.1 ppm). Moreover, both the NMR and UV−vis spectra of **5Zn** showed no dependence upon concentration or temperature.

Discussion

Our aim was to gain a good understanding of the spectroscopic characteristics of relevant Ru−PyP compounds before undertaking the synthesis of more complicated supramolecular arrays, such as molecular squares of PyPs held together by ruthenium complexes. ^{1}H NMR spectroscopy proved particularly useful for characterizing the Ru−PyP complexes described above. Coordination to Ru affected mainly the resonances of the pyridyl ring(s) of PyPs, causing downfield shifts (H2,6 signals from 0.3 to 0.9 ppm, H3,5 from 0.03 to 0.18 ppm). The resonances of the protons on the phenyl rings, when present, were not particularly influenced by coordination, except in *cis*

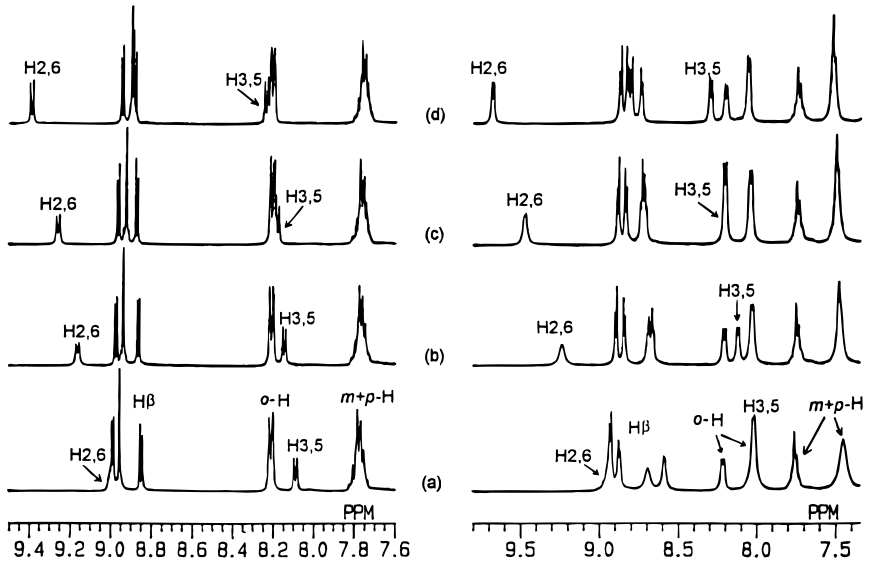

Figure 7. Effect of the addition of CD_3OD on the ^1H NMR MPyP signals of *cis,cis,cis*-$RuCl_2(Me_2SO)_2(CO)$(Zn·MPyP) (**1Zn**) (left) and *trans,-cis,cis*-$RuCl_2(Me_2SO)_2$(Zn·MPyP)$_2$ (**4Zn**) (right). Left: [**1Zn**] = 2.50 mM (a), + 2 μL of CD_3OD (b), + 4 μL of CD_3OD (c), + 8 μL of CD_3OD (d). Right: [**4Zn**] = 2.50 mM (a), + 8 μL of CD_3OD (b), + 16 μL of CD_3OD (c), + 64 μL of CD_3OD (d).

disubstituted complexes (see below). The resonances of the pyrrole protons were particularly informative about the geometry of the porphyrin, while the Me_2SO signals, when present, gave information about the coordination environment. Spectroscopic data (IR, ^{13}C NMR) involving the carbonyl and chloride ligands provided further evidence for the unambiguous assignment of the product geometry. In general, the UV−vis and fluorescence spectra of the complexes were similar to those of the corresponding unbound PyPs, suggesting that coordination to Ru does not significantly affect the electronic properties of the porphyrin ring. This was not true for the *cis*-disubstituted complex *trans,-cis,cis*-$RuCl_2(Me_2SO)_2(MPyP)_2$ and, to a minor extent, *trans,-cis,cis*-$RuCl_2(Me_2SO)(CO)(MPyP)_2$, where the reduced ϵ/MPyP of the Soret band and the decreased intensity of the emission band suggest some electronic coupling between the two *cis*-porphyrins.[24] A more detailed investigation of the photophysical properties of such complexes is the subject of an ongoing collaboration.

In particular, one NMR feature of the *cis*-disubstituted MPyP species is worth discussing in more detail. In the ^1H NMR spectrum of, for example, *trans,cis,cis*-$RuCl_2(Me_2SO)_2(MPyP)_2$, there are two sets of multiplets for the phenyl protons (i.e. *o*-H and *m*+*p*-H) of the two *cis* MPyP ligands. The two sets are identified by the relative intensities and by crosspeaks in the COSY spectrum (Figure 8). The two multiplets of the minor set, which integrate for 4 and 6 protons, respectively, are almost unshifted compared to MPyP; these are assigned to *o*-H and *m*+*p*-H of the phenyl ring *trans* to the pyridyl ring (position 15). The signals of the major set, which integrate for 8 and 12 protons, respectively, and are shifted upfield by about 0.2 ppm, are assigned to the two phenyl rings *cis* to the pyridyl ring (positions 10 and 20). The upfield shift is probably caused by the rotation of MPyP about the Ru−pyridyl axis, which brings the phenyl rings at the 10,20-positions into the shielding cone of the adjacent porphyrin ring. The relatively small extent of the upfield shift suggests that the two porphyrins rotate freely and that the average time spent in the orientations inducing mutual shielding is rather short. A very similar NMR pattern was found also in the analogs, *trans,cis,cis*-$RuCl_2(CO)_2(MPyP)_2$ and *trans,cis,cis*-$RuCl_2(Me_2SO)(CO)(MPyP)_2$, but not in the other complexes bearing a single porphyrin. We believe that the pattern is quite characteristic of two mutually *cis* pyridylporphyrins in free rotation about the metal−pyridyl axis. Contradictory data, presented without comment, have been reported for MPyPs coordinated to adjacent sites in square planar centers.[25] For example, a splitting of the phenyl resonances, an NMR pattern similar to that found here, was observed in the tetramers [Pt(MPyTP)$_4$](OTf)$_2$ (MPyTP = 5-(4-pyridyl)-10,-15,20-tritolylporphyrin; OTf = triflate) and [Pt(Zn·MPyP)$_4$]-(OTf)$_2$. However, the opposite, i.e. upfield shift of the resonances of the phenyl ring at the 15-position, was reported for the similar tetramer [Pt(MPyTP)$_4$](BF$_4$)$_2$, and apparently no splitting of the phenyl resonances occurred in the dimers *cis*-Pt(MPyP)$_2$Cl$_2$ and *cis*-Pt(MPyTP)$_2$Cl$_2$.[24,25]

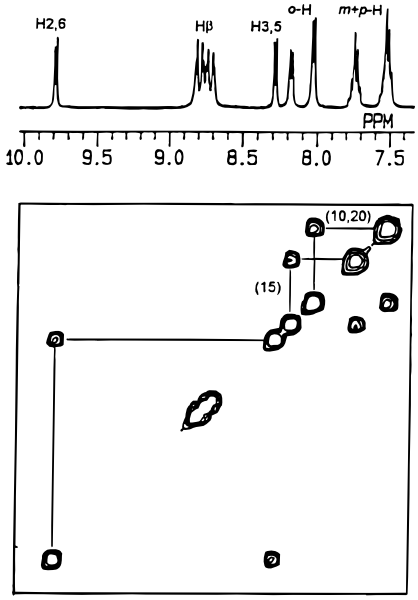

Figure 8. Downfield region of the H−H COSY spectrum of *trans,-cis,cis*-$RuCl_2(Me_2SO)_2(MPyP)_2$ (**4**).

We also found NMR evidence that the Ru−Zn·PyP complexes bearing residual Me_2SO units, such as *cis,cis,cis*-$RuCl_2$-$(Me_2SO)_2(CO)$(Zn·MPyP), *trans,cis,cis*-$RuCl_2(Me_2SO)_2$(Zn·-MPyP)$_2$, and (Zn·TPyP)[*cis,cis,cis*-$RuCl_2(Me_2SO)_2(CO)]_4$ self-assemble spontaneously in solution. Since the effect does not occurr in *trans,cis,cis*-$RuCl_2(CO)_2$(Zn·MPyP)$_2$, we believe that the oxygen atom of a Me_2SO ligand of one molecule and the zinc of another molecule interact. Accordingly, the intermolecular interaction brings the Me_2SO of one molecule into the

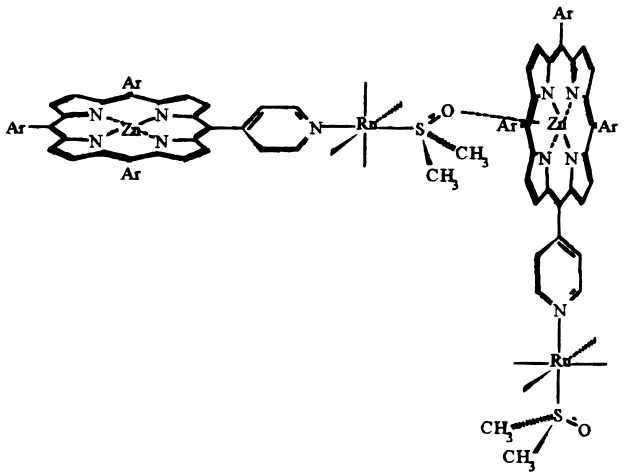

Figure 9. Schematic drawing of the self-assembling process.

shielding cone of the porphyrin ring of another molecule, inducing an upfield shift of all resonances in the NMR spectrum (Figure 9). However, the relatively small upfield shift of Me_2SO resonances and their broadening suggest that the interaction is not particularly strong and rather labile. Consistent with this hypothesis, the extent of aggregation in $CDCl_3$ solution is diminished, not only by an increase in temperature or a decrease in concentration, but also by addition of a coordinating solvent such as methanol, which can successfully compete for Zn with the oxygen atom of Me_2SO. Combined UV−vis and ^1H NMR evidence suggested that, in chloroform, *cis,cis,cis*-$RuCl_2(Me_2SO)_2(CO)$(Zn·MPyP) and *trans,cis,cis*-$RuCl_2(Me_2SO)_2$(Zn·MPyP)$_2$ self-assemble above 10^{-6} M. The self-assembling process of (Zn·TPyP)[*cis,cis,cis*-$RuCl_2(Me_2SO)_2(CO)]_4$ starts at concentrations lower than 10^{-7} M, and hence, this tetramer is barely soluble in chloroform. However, it can be dissolved by addition of small amounts of methanol, which presumably binds to Zn and disrupts the supramolecular array. The NMR spectra of both *cis,cis,cis*-$RuCl_2(Me_2SO)_2(CO)$(Zn·MPyP) and *trans,cis,*-*cis*-$RuCl_2(Me_2SO)_2$(Zn·MPyP)$_2$ show that the upfield shift of the MPyP resonances is roughly proportional to the distance of the protons from Ru; i.e., it is maximum for H2,6 and then gradually decreases for protons further removed. This observation suggests that bound MPyP enters head-on into the shielding cone of another unit, as schematically depicted in Figure 9, and therefore assemblies with face-to-face porphyrins are not likely to play a major role.

The interaction between the oxygen atom of S-bonded sulfoxide and a metal species is not completely without precedent; we have observed it in solution between oligomers of zinc porphyrins and inert Ru−Me_2SO complexes.[18] Previous reports concerned Ru−sulfoxide complexes in the solid state.[34] However, this interaction might not occur when Me_2SO is bound to other metal ions; in fact, no significant difference was reported between the ^1H NMR $CDCl_3$ spectra of *cis*-Pt(Me_2SO)(MPyP)-Cl_2 and its zinc derivative *cis*-Pt(Me_2SO)(Zn·MPyP)Cl_2.[25]

Previous examples of porphyrin self-assembly involved pyridine−metal coordination. In most cases, both the pyridine ligand and the metal acceptor atom inside the porphyrin belonged to a single molecule,[14d,16,17] but there are very recent reports in which these moieties are located in separate molecules.[35,36] In this case either two contemporaneous pyridine−metal interactions occurred[35] or another interaction, such as that between boronic acid and a diol, was needed.[36] The self-assembling process of M·PyPs bearing peripheral Ru−Me_2SO complexes represents a new category.

Our study reveals two unprecedented features. First, the two reactive centers belong to the same molecule, which is nevertheless a coordination compound; this allows the introduction of a second metal center, in this case ruthenium, into the supramolecular array. Second, a new kind of noncovalent interaction is used, which takes advantage of the residual basicity of the oxygen atom of S-bonded sulfoxide ligands. Even though this particular interaction might not be strong enough for producing stable aggregates, such aggregates could be achieved by changing the nature of the basic site in the peripheral metal moiety.

Conclusions and Future Prospects

The reactivity of the PyPs with the Ru−Me_2SO precursors closely reflects that already observed by us with simpler N-donor ligands. In other words, the number and the fixed stereochemical relationship of the coordination sites of these Ru precursors are predictable. This chemistry was successfully exploited for controlling the geometric configuration of supramolecular Ru−PyP assemblies. Moreover, most of the above complexes are quite soluble in organic solvents such as $CHCl_3$ (also when PyPs are metalated) and are very robust in solution, where they remain intact for weeks. To our knowledge, they represent the first example of systematic and rational approach to the synthesis of isolated and well-characterized octahedral complexes of pyridylporphyrins. Compared to previous examples which mainly had peripheral square planar Pt(II) and Pd(II)−PyP moieties,[24,25] the two additional coordinated "spectator" ligands in octahedral complexes might prove advantageous for a series of reasons. These ligands might allow the following: better fine-tuning of the properties of the metal; greater solubility in organic solvents; useful extra spectroscopic handles for the characterization; additional avenues for assembling more extended structures.

As a logical extension of the synthetic results obtained by us with MPyP, reaction of the *cis*-coordinating ruthenium precursors, i.e. *trans*-$RuCl_2(Me_2SO)_4$ and its carbonyl derivatives, with equimolar amounts of *cis* or *trans*-DPyP might be expected to yield 2 + 2 or 4 + 4 molecular squares, respectively, similar to those reported by Lehn with square planar Pt(II) and Pd(II) complexes.[24] Some of the new complexes are indeed good models for the basic components of such supramolecular assemblies. The *cis*-disubstituted MPyP species *trans,cis,cis*-$RuCl_2(Me_2SO)_2(MPyP)_2$, *trans,cis,cis*-$RuCl_2(CO)_2(MPyP)_2$, and *trans,cis,cis*-$RuCl_2(Me_2SO)(CO)(MPyP)_2$ can be viewed as the corners of 4 + 4 or 2 + 2 molecular squares. The *trans*-dimer (*trans*-DPyP)[*cis,cis,cis*-$RuCl_2(Me_2SO)_2(CO)]_2$ is a model for the side of a 4 + 4 square. On the other hand, the *cis*-dimer (*cis*-DPyP)[*cis,cis,cis*-$RuCl_2(Me_2SO)_2(CO)]_2$ is a good model

(34) Jaswal, J. S.; Yapp, D. T. T.; Rettig, S. J.; James, B. R.; Skov, K. A. *J. Chem. Soc., Dalton Trans.* **1992**, 1528.
(35) Hunter, C. A.; Hyde, R. K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1936.
(36) Sarson, L. D.; Ueda, K.; Takeuchi, M.; Shinkai, S. *Chem. Commun.* **1996**, 619.
(37) Abbreviations: Tetraphenylporphyrin (TPP); 5-(4-pyridyl)-10,15,20-triphenylporphyrin (MPyP); 5,10-bis(4-pyridyl)-15,20-diphenylporphyrin (*cis*-DPyP); 5,15-bis(4-pyridyl)-10,20-diphenylporphyrin (*trans*-DPyP); 5,10,15-tris(4-pyridyl)-20-phenylporphyrin (TrPyP) and 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP).
(38) According to elemental analysis, **5Zn** has some methanol of crystallization. The ^1H NMR spectrum of **5Zn** in $CDCl_3$ confirmed the presence of CH_3OH (sharp doublet at 3.14 ppm coupled with a well-resolved quartet at 0.51 ppm in a 3:1 intensity ratio). Its resonances are remarkably shifted upfield compared to those of CH_3OH in a $CDCl_3$ solution of comparable concentration (sharp doublet at 3.49 ppm and quartet at 0.94 ppm). This is ascribable to the very labile binding of methanol to Zn, which brings the molecule inside the anisotropic shielding cone of the porphyrin.

for the other corner of 2 + 2 molecular squares. The inequivalence of the phenyl resonances in *cis*-disubstituted MPyP species as described above might allow us to distinguish in solution between open chain oligomers, where rotation would be allowed and the separation of the phenyl resonances is expected, and 2 + 2 closed arrays, where rotation would be impossible.

We also showed that Ru−Me_2*S*O−M·PyP adducts are endowed with self-assembling properties and thus represent a new type of building block, with the metalloporphyrin and the basic site bound to the same coordination compound. Regardless of the specific nature of the basic site, this type of building block offers some general advantages potentially exploitable in the design of new supramolecular porphyrin arrays. In fact, both the number of acidic and basic sites can be changed, together with their relative geometry. Indeed, the strength of the interaction can be rather easily tuned by changing the electron donor capability of the basic site. This capability can be modified either by changing the metal center or, as we have shown previously for the Me_2*S*O−Zn case,[18] the donor/acceptor properties of the other ligands.

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Supporting Information Available: Listings of elemental analyses and electronic absorption, selected IR, and ^{13}C and ^{1}H NMR spectral data (6 pages). Ordering information is given on any current masthead page.

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