Two-Point Self-Coordination of a Dizinc(II) Bispyridylporphyrin Ruthenium Complex Leading Selectively to a Discrete Molecular Assembly: Solution and Solid-State Characterization

Elisabetta Iengo,*[a] Ennio Zangrando,*[a] Silvano Geremia,[a] Roland Graff,[b] Bruno Kieffer,[c] and Enzo Alessio[a]

Abstract: The dizinc(II) bispyridylporphyrin ruthenium complex *trans,cis,cis*-[$RuCl_2(CO)_2(Zn\cdot 4'$-*cis*DPyP$)_2$] (**1Zn**, 4′-*cis*DPyP = 5,10-bis(4′-pyridyl)-15,20-diphenylporphyrin) features two donor (the uncoordinated 4′-N(py) atoms) and two acceptor (the Zn atoms) sites and is thus a building block suited for two-point coordination. ^1H NMR spectroscopy indicates that **1Zn** self-assembles in solution through Zn–4′-N(py) interactions to yield selectively a highly symmetrical discrete species, in which all donor and all acceptor sites of **1Zn** are mutually saturated. Single-crystal X-ray analysis established that this adduct is a dimeric species, $(\mathbf{1Zn})_2$, with a global S_4 symmetry, in which the four porphyrins have a propeller-like arrangement. The dimeric species $(\mathbf{1Zn})_2$ is a *meso* form derived from the combination of two **1Zn** units with opposite helical chirality. The geometry of this highly symmetrical tetraporphyrin assembly in solution, as determined by NMR spectroscopy, is essentially the same as that found in the solid state. Thus **1Zn** is an unprecedented example of metal-containing self-complementary building block that selectively recognizes itself through four Zn–N(py) interactions, and thus yields a very stable and symmetrical dimeric species, $(\mathbf{1Zn})_2$, that features four porphyrins and six metal atoms (two Ru and four Zn).

Keywords: porphyrins · metalloporphyrins · self-assembly · self-coordination · supramolecular chemistry · zinc

Introduction

There is substantial recent interest worldwide in the construction of multiporphyrin assemblies that can either mimic naturally occurring multichromophore aggregates, such as the photosynthetic reaction center and the light-harvesting complex of purple bacteria, or that can be used as electron- and/or energy-transfer molecular devices for advanced technological tasks. The metal-mediated self-assembly approach, which exploits the formation of coordination bonds between peripheral basic site(s) on the porphyrins and metal centers, has recently allowed the design and preparation of sophisticated supramolecular architectures whose complexity and function begin to approach the properties of naturally occurring systems.[1]

A particularly fascinating field of investigation within this general topic concerns the design and construction of ordered structures formed by a single component interacting with itself (*self-coordination*). Most of the examples reported to date concern the one-point self-coordination of metalloporphyrins bearing one peripheral N-donor site, usually a pyridyl or imidazolyl moiety; with few exceptions,[2] the metal inside the porphyrin has only one axial coordination site available (e.g. Zn^{II} or $Ru^{II}(CO)$). The nature of the resulting architectures, either discrete macrocyclic species[3, 4] or linear stairlike oligomers/polymers,[5] depends mainly on the relative geometry of the porphyrin plane (acceptor site) and of the donor site in the monomer. Concentration plays also a crucial role in affecting the equilibria between discrete and polymeric species.[5a, 6, 7] Only very recently, Kobuke and co-workers described the two-point self-coordination of a dizinc(II) bisimidazolylporphyrin dimer, which leads to a mixture of linear oligomers.[8]

---

[a] Dr. E. Iengo, Prof. E. Zangrando, Dr. S. Geremia, Prof. E. Alessio
Dipartimento di Scienze Chimiche
Università di Trieste
Via L. Giorgieri 1, 34127 Trieste (Italy)
Fax: (+39) 40 5583903
E-mail: iengo@dsch.univ.trieste.it, zangrand@dschsun3.univ.trieste.it

[b] Dr. R. Graff
Service commun de RNM
Faculté de Chimie del'Université Louis Pasteur
1, rue Blaise Pascal, 67000 Strasbourg (France)

[c] Dr. B. Kieffer
Groupe de RMN, UMR 7104 du CNRS
Ecole Superieure de Biotechnologie de Strasbourg
Boulevard Sebastien Brant, Pole API
67400 Strasbourg-Illkirch (France)

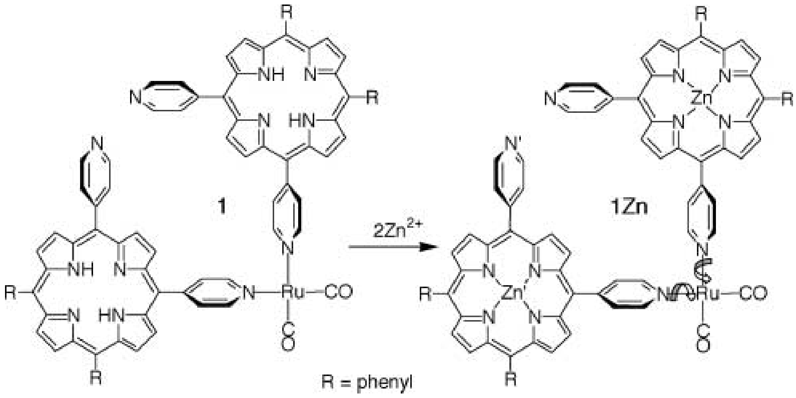
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

0947-6539/02/0820-4670 $ 20.00+.50/0

We report here the first example of two-point self-coordination that leads to a discrete supramolecule: a dizinc(II) bispyridylporphyrin ruthenium complex selectively recognizes itself through four Zn–N(py) interactions, and thus yields a very stable dimeric species. The geometry of this tetraporphyrin assembly in the solid state, determined by single-crystal X-ray diffraction, is essentially the same as that deduced by NMR spectroscopy in solution.

Results and Discussion

The bis-(4′-pyridyl)porphyrin ruthenium adduct *trans,cis,cis*-[$RuCl_2(CO)_2$(4′-*cis*DPyP)$_2$] (**1**, Scheme 1, 4′-*cis*DPyP = 5,10-bis(4′-pyridyl)-15,20-diphenylporphyrin), which has one residual unbound 4′-N(py) ring on each of the two *cis*-coordinated 4′-*cis*DPyP units, is a building block suited for two-point coordination.[9] We anticipated that insertion of Zn^{2+} into the two porphyrins of **1** would yield an unprecedented example of metal-containing building block, *trans,cis,cis*-[$RuCl_2(CO)_2$(Zn · 4′-*cis*DPyP)$_2$] (**1Zn**), featuring two donor and two acceptor sites whose relative orientation depends on the conformational motions of the two zinc porphyrins about the Ru–N bonds (Scheme 1). Models show that when in **1Zn** the absolute value of the sum of the two ideal torsion angles $N(py)_{free}\cdots Zn\cdots Ru\cdots Zn'$ (ϕ) and $N'(py)_{free}\cdots Zn'\cdots Ru\cdots Zn$ (ϕ') is < 90°, the two 4′-N(py) atoms have a mutual orientation that we define as *convergent* (Figure 1); otherwise their are *divergent* and are more likely to generate open-chain polymeric species by self-coordination. Moreover, for orientations of the two porphyrins other than $\phi = -\phi'$, **1Zn** acquires helical chirality (Λ/Δ) and combination of **1Zn** units with either the same or opposite chirality can occur, generating different species.



Scheme 1. Schematic drawing of *trans,cis,cis*-[$RuCl_2(CO)_2$(4′-*cis*DPyP)$_2$] (**1**) and of the zincated derivative **1Zn** (top view along the Cl–Ru–Cl bond system, Cl atoms omitted for clarity).

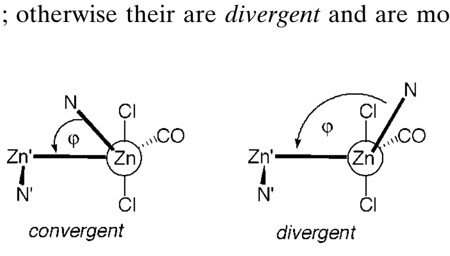


Figure 1. Schematic drawing of **1Zn** viewed along the Zn ··· Ru bond axis evidantiating the $N(py)_{free}\cdots Zn\cdots Ru\cdots Zn'$ torsion angle ϕ ($\phi' = 0°$); only part of the coordination sphere of the ruthenium atom on the back (indicated with a circle) is represented. A *convergent* (left, $|\phi + \phi'| < 90°$) and a *divergent* (right, $|\phi + \phi'| > 90°$) orientation of the two free 4′N(py) atoms are shown.

In the ^1H NMR spectrum of the raw product obtained by treatment of **1** with excess zinc acetate sharp resonances of a discrete self-coordinated product ($(\mathbf{1Zn})_n$) are largely predominant; broad peaks of minor intensities are attributed to oligomeric species (see Supporting Information). The discrete product was obtained in pure form by chromatography on a silica column, where it runs as a single band (it is significantly less polar than **1**, $R_f = 0.82$ versus 0.28 for **1**).

The $CDCl_3$ NMR spectrum of $(\mathbf{1Zn})_n$ shows sharp resonance signals in the downfield region and four relatively broad resonance signals at higher fields, which become sharp on lowering the temperature below 0 °C (Figure 2). Attributions were performed by means of 2D COSY and NOESY-EXSY spectra (see Supporting Information). Overall, the following observations and conclusions can be drawn from the NMR spectra: 1) there are no signals for uncoordinated pyridyl rings; each 4′-N(py) ring of **1Zn** is bound either to Ru or to the Zn atom inside another porphyrin (Figure 3); axial coordination to a zinc–porphyrin induces typical upfield shifts due to the anisotropic shielding cone of the porphyrin ring, in particular for the protons of the 4′-N(py) ring bound to Zn and for the neighboring βH protons (Figure 2 and Figure 3).[7, 10–12] Thus, in agreement with its high mobility on silica gel, $(\mathbf{1Zn})_n$ has all donor and all acceptor sites of each **1Zn** unit mutually saturated through Zn–4′-N(py) interactions. 2) There is only one set of porphyrin resonances, that is all the porphyrins in $(\mathbf{1Zn})_n$ are equivalent to each other, indicating a highly symmetrical architecture. As anticipated by the different coordination of the two 4′-N(py) rings on each 4′-*cis*DPyP unit (one bound to Ru and the other to Zn), each single porphyrin is in an asymmetric environment (Figure 3). Accordingly, eight resolved resonances, connected pairwise in the H–H COSY spectrum, are found for the pyrrole protons. 3) With the exception of the *meta* and *para* phenyl protons, each aromatic proton has its own well resolved resonance. For example, the resonances of H2**Ru** and H6**Ru** are about 0.7 ppm apart from one another (Figure 2); these twelve resonance signals are pairwise connected by strong exchange cross peaks in the NOESY-EXSY spectrum.

The high symmetry of $(\mathbf{1Zn})_n$ is apparent also from the $^{13}C\{^1H\}$ NMR spectrum of a ^{13}CO-enriched sample, in which a single carbon resonance signal for the equivalent CO groups is observed at $\delta = 195.0$ ppm. In the IR spectrum in chloroform (of the same sample) two carbonyl stretching bands are

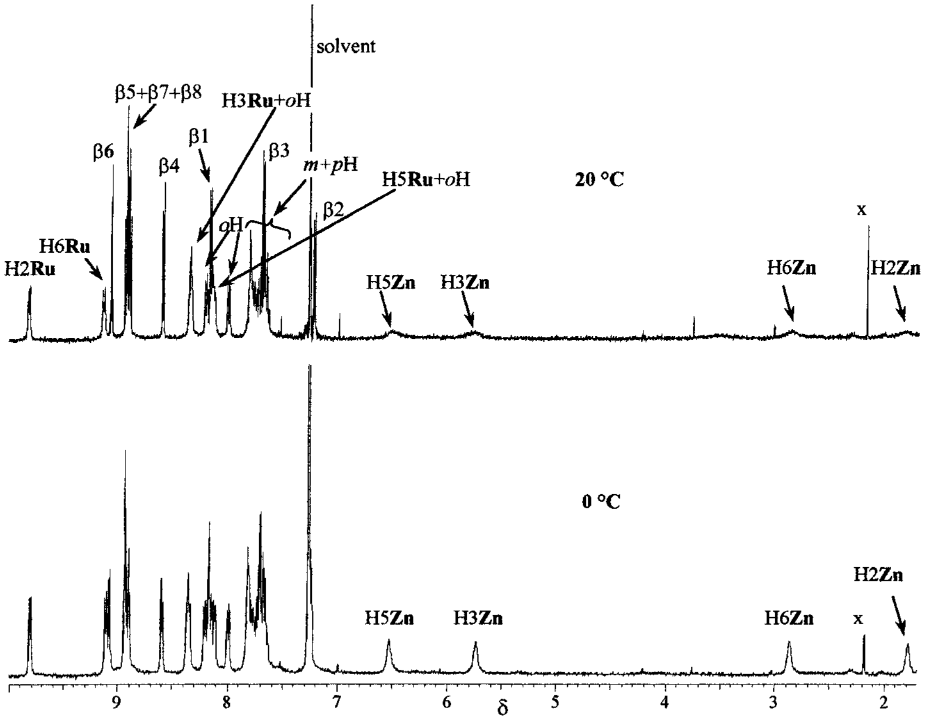


Figure 2. ^{1}H NMR spectra ($CDCl_3$) of $(\mathbf{1Zn})_n$ at room temperature (top) and at 0 °C (bottom). See Figure 3 for labeling scheme. An impurity is marked with X.

detected at 2025 and 1968 cm^{-1}, as expected for a *cis* geometry of the two CO molecules on each ruthenium unit.

The visible absorption spectrum of $(\mathbf{1Zn})_n$ (see Supporting Information) is quite similar to that of the closest model in which no self-coordination occurs: the bisporphyrin ruthenium complex with zinc monopyridylporphyrin (Zn · 4′-MPyP), *trans,cis,cis*-[$RuCl_2(CO)_2$(Zn · 4′-MPyP)$_2$] (**2 Zn**).[13] The axial coordination of 4′-N(py) sites to the zinc porphyrins in $(\mathbf{1Zn})_n$ induces a typical bathochromic shift of about 10 nm for the Soret band compared to **2 Zn**, which becomes even larger (ca. 15 nm) for the Q bands.

The single-crystal X-ray analysis of $(\mathbf{1Zn})_n$ established that the compound is actually a dimeric species, in which all four 4′-N(py) and all four Zn sites of two **1 Zn** units are mutually saturated. Two crystallographically independent $(\mathbf{1Zn})_2$ adducts were detected in the unit cell. In each of them the four porphyrins have a propeller-like arrangement, with a global S_4 symmetry (the improper rotation axis passes through the ruthenium ions) (Figure 4 and Figure 5). The adduct is thus a *meso* form derived from the combination of two *convergent* **1 Zn** units with opposite helical chirality. In each **1 Zn** unit of $(\mathbf{1Zn})_2$ the ideal $\mathrm{N(py)_{Zn}\cdots Zn\cdots Ru\cdots Zn'}$ and $\mathrm{N'(py)_{Zn}\cdots Zn'\cdots Ru\cdots Zn}$ torsion angles (ϕ and ϕ') are close to 40° (synclinal arrangement), both of positive sign in one unit, negative in the other. The four Zn ions, which have a square-pyramidal environment, occupy the vertices of an irregular tetrahedron, with an intermetallic separation in each **1 Zn** unit of 12.46 Å (mean value), while the distances involving the zinc of the two **1 Zn** units are shorter and average to 9.83 Å. Each Zn ion is displaced by about 0.3 Å from the mean porphyrin plane towards the apical pyridine donor. The Ru ions display a distorted octahedral geometry and are 19.6 Å far apart. In order to achieve the two-point self-coordination, the porphyrin planes of each **1 Zn** unit form a dihedral angle in the narrow range of 42–45°, while the angles between the planes of axially connected porphyrins vary from 76 to 89°. An estimation of the molecular size of $(\mathbf{1Zn})_2$ is provided by the distances between the carbonyl oxygen atoms of the two Ru ions, of about 24.0 Å, which are comparable with those between the outmost phenyl carbon atoms. In one of the two crystallographically independent units the small internal cavity is partially occupied by two chloroform molecules.

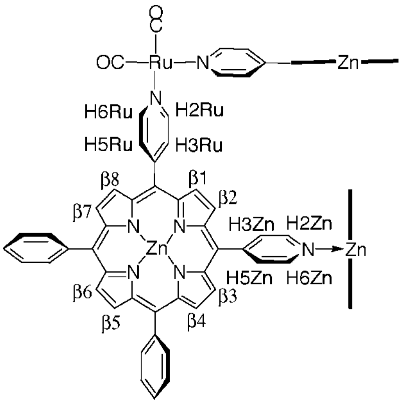


Figure 3. Schematic drawing representing the coordination environment of any zincated porphyrin within $(\mathbf{1Zn})_n$ (top view along the Cl–Ru–Cl bond system, Cl atoms omitted for clarity). Side-viewed porphyrins are represented with a thick line.

The solid-state structure explains well the NMR spectrum of $(\mathbf{1Zn})_2$ in $CDCl_3$, indicating that the same architecture is maintained in solution.[14] The C_2 and S_4 symmetry axes passing through the two Ru atoms make all porphyrins equivalent (and the two Ru complexes as well). Each *meso* aromatic ring has one side oriented towards the inside (*endo*) and the other towards the outside (*exo*) of the capsule; thus the *endo* protons (and those of the inner pyridyl rings in particular) are more shielded by the combined effect of the four porphyrins and therefore resonate more upfield than the corresponding *exo* protons. The two sides of each *meso* aromatic ring are exchanged by rotation about the C_{meso}–C_{ring} bond, which is slow on the NMR time scale at room temperature already.

Both NMR and UV/Vis spectra were found to be concentration independent in the range from 10^{-3} to 10^{-6} M, indicating that the disassembly of $(\mathbf{1Zn})_2$ is negligible even at the lowest concentration examined.

NMR competition experiments were performed by addition of either acidic or basic building blocks to solutions of

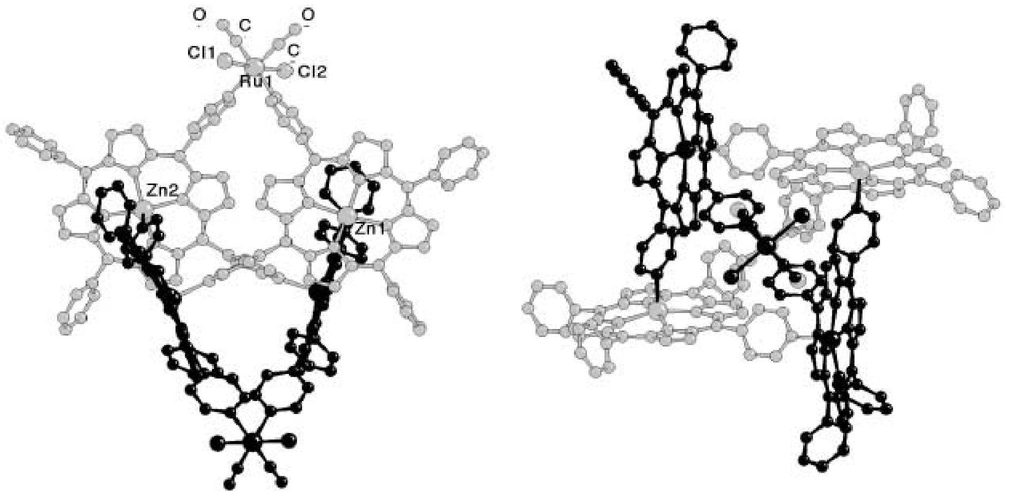


Figure 4. Two perspective views of the solid state molecular structure of $(\mathbf{1Zn})_2$; the right view is along the S_4 axis. For clarity the two **1Zn** units have different shades.

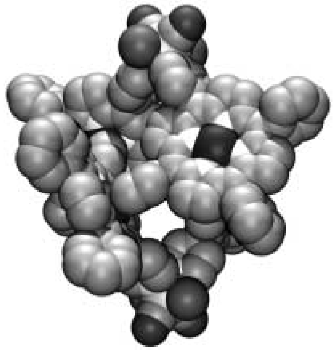


Figure 5. Space-filling representation of the left view of Figure 4.

$(\mathbf{1Zn})_2$ in $CDCl_3$. We showed that titration of $(\mathbf{1Zn})_2$ with [Pd(dppp)-$(OTf)_2$] (dppp = 1,3-bis-(diphenylphosphanyl)-propane, OTf = trifluoromethanesulfonate = triflate) yields quantitatively the hetero-trinuclear molecular square [Pd(dppp)-{*trans,cis,cis*-[$RuCl_2(CO)_2$-(Zn·4′-*cis*DPyP)$_2$]}]$(OTf)_2$.[9] Addition of incresing amounts of 4-picoline (4-pic) up to 4-pic/$(\mathbf{1Zn})_2$ ≈ 0.8 induced a progressive broadening of the pyridyl resonances of $(\mathbf{1Zn})_2$, indicating the occurrence of exchange processes.[15] Further additions of 4-pic left the spectrum substantially unchanged. Column purification of the final mixture (4-pic/$(\mathbf{1Zn})_2$ ≈ 2) yielded back $(\mathbf{1Zn})_2$.

Conclusion

In conclusion, *trans,cis,cis*-[$RuCl_2(CO)_2$(Zn·4′-*cis*DPyP)$_2$] (**1Zn**) is an unprecedented example of a bisporphyrin self-complementary building block that recognizes itself through four Zn-4′-N(py) axial interactions, and thus yields a discrete dimeric assembly, $(\mathbf{1Zn})_2$. The high degree of cooperativity of such interactions accounts for the good selectivity found for the formation of the discrete species $(\mathbf{1Zn})_2$ over polymeric products and for its high stability in solution. We aim now to investige the self-assembling properties of closely related building blocks featuring two donor and two acceptor binding sites; in particular we plan to maintain the frame of the dizinc(II) bispyridylporphyrin ruthenium complex intact, and assess the effect of a change in the position of the N(py) atom (3′ versus 4′ pyridylporphyrins) or in the geometry of the bispyridilporphyrin (4′-*trans*DPyP instead of 4′-*cis*DPyP) on the nature of the self-assembled product.

Experimental Section

Column chromatography was performed on 40–63 µm mesh silica gel (BDH). A sample of ^{13}CO was purchased from Aldrich. UV/Vis spectra were obtained on a Jasco V-550 spectrometer in quartz cells, using CH_2Cl_2 freshly distilled over dry $CaCl_2$ as solvent. ^1H NMR and ^{13}C NMR spectra were recorded at 400 and 100.5 MHz, respectively, on a JEOL Eclipse 400 FT instrument. All spectra were run in $CDCl_3$ (Aldrich). Proton peak positions were referenced to the peak of residual non-deuterated chloroform set at $\delta = 7.26$ ppm. Carbon peak positions were referenced to the central peak of chloroform set at $\delta = 77.0$ ppm. Assignments were made with the aid of 2D correlation spectroscopy (H-H COSY) and of 2D exchange spectroscopy (EXSY) experiments as detailed in the text; a mixing time of 500 ms was used for EXSY experiments. Solution ($CHCl_3$) infrared spectra were recorded in 0.1 mm cells with NaCl windows on a Perkin-Elmer 983G spectrometer.

Compound **1** was prepared and purified according to the literature procedure.[9]

1Zn: Compound **1** (10 mg, 5.9×10^{-3} mmol) dissolved in $CHCl_3$ (5 mL) was treated for 48 h with a fourfold excess of zinc acetate dissolved in methanol (2 mL). After removal of the solvent, the solid residue was washed throughly with water, methanol, and then with diethyl ether and vacuum-dried (yield of isolated product about 70%). It was purified by chromatography on a silica gel column eluted with chloroform (first band) (yield of isolated product about 60%); part of the reaction mixture remained adsorbed on the top of the column. UV/Vis spectrum (λ_{max} ($\varepsilon \times 10^5$) in CH_2Cl_2: 428.0 (Soret, 8.37), 563.0 (0.59), 603.5 nm (0.28 $cm^{-1}\,M^{-1}$); ^1H NMR spectrum ($CDCl_3$): $\delta = 9.82$ (d, 4H; H2**Ru**, *exo*), 9.14 (d, 4H; H6**Ru**, *endo*), 9.06 (d, 4H; β6), 8.91 (m, 12H; $\beta5+7+8$), 8.59 (d, 4H; β4), 8.33 (m, 8H; H3**Ru**, *exo* + *o*H *exo*), 8.21 (d, 4H; *o*H, *exo*), 8.18 (d, 4H; β1), 8.13 (m, 8H; H5**Ru**, *endo* + *o*H *endo*), 8.00 (d, 4H; *o*H, *endo*), 7.67 (m, 28H; *m* + *p*H + β3), 7.22 (d, 4H; β2), 6.50 (br, 4H; H3**Zn**, *exo*), 5.77 (br, 4H; H5**Zn**, *endo*), 2.86 (br, 4H; H2**Zn**, *exo*), 1.82 (br, 4H; H6**Zn**, *endo*).

X-ray crystallography: Crystals of $(\mathbf{1Zn})_2$ were obtained by slow diffusion of *n*-hexane into a solution in $CHCl_3$. Crystal data: $C_{186}H_{122}N_{24}O_4Cl_{37}Zn_4$-$Ru_2$, $M_r = 4532.35$, triclinic, space group $P1 <$ Ü →, $a = 19.634(4)$, $b = 31.311(5)$, $c = 37.627(5)$ Å, $\alpha = 102.72(3)$, $\beta = 93.86(3)$, $\gamma = 106.18(3)°$, $V = 21465(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.403\ mg\,m^{-3}$, $\mu = 1.092\ mm^{-1}$, $F(000) = 9100$, $2\theta_{max} = 41.5°$. Reflections measured = 71284, unique 41247 [$R_{int} = 0.075$], reflections $I > 2.0\sigma(I) = 27136$, parameters = 2322, $R1$ [$I > 2\sigma(I)$] = 0.1304, $wR2 = 0.3573$. Data collection performed at the X-ray diffraction beamline of Elettra Synchrotron, Trieste (Italy), on a 30 cm MAR2000 image plate with a monochromatic wavelength ($\lambda = 0.7100$ Å), using the rotating crystal method. The structure was solved by direct method and Fourier analyses (SHELXS-97) and refined by full-matrix least-squares based on F^2 using SHELXL-97.[16a] All the calculations were performed by using the WinGX System, Version 1.64.[16b] Of the 22 $CHCl_3$ and 0.5 *n*-hexane solvent molecules per complex unit, most were located on the difference Fourier map, others were included for density calculation by taking into account the accessible voids in the unit cell, as obtained through utility VOID included in the Platon package.[16c]

CCDC-183728 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44)1223-336033; or deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was supported by Italian CNR (grants C00B91D and G000951). We thank Johnson Matthey for a loan of hydrated $RuCl_3$. The CNR staff at ELETTRA is acknoweldged for help in the use of the facility supported by CNR and by Elettra Scientific Division.

---

[1] a) J.-C. Chambron, V. Heitz, J.-P. Sauvage in *The Porphyrin Handbook*, *Vol. 6* (Eds.: K. M. Kadish, K. M. Smith, R. Guillard), Academic Press, **2000**, Chapter 40; b) J. Wojaczynski, L. Latos-Grazynski, *Coord. Chem. Rev.* **2000**, *204*, 113–171.

[2] a) Y. Kokube, H. Miyaji, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 3563–3569; b) U. Michelsen, C. A. Hunter, *Angew. Chem.* **2000**, *112*, 780–783; *Angew. Chem. Int. Ed.* **2000**, *39*, 764–767.

[3] a) C. A. Hunter, L. D. Sarson, *Angew. Chem.* **1994**, *106*, 2424–2426; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2313–2316; b) R. T. Stibrany, J. Vasudevan, S. Knapp, J. A. Potenza, T. Emge, H. J. Sugar, *J. Am. Chem. Soc.* **1996**, *118*, 3980–3981; c) A. K. Burrell, D. L. Officer, D. C. W. Reid, K. Y. Wild, *Angew. Chem.* **1998**, *110*, 122–125; *Angew. Chem. Int. Ed.* **1998**, *37*, 114–117; d) Y. Kobuke, H. Miyaji, *J. Am. Chem. Soc.* **1994**, *116*, 4111–4112.

[4] K. Funatsu, A. Kimura, T. Imamura, Y. Sasaki, *Chem. Lett.*, **1995**, 765–766.

[5] a) M. O. Senge, K. M. Smith, *J. Chem. Soc. Chem. Commun.* **1994**, 923–924; b) A. M. Shachter, E. B. Fleischer, R. C. Haltiwanger, *Chem. Commun.* **1988**, 960–961; c) M. J. Gunter, G. M. McLaughlin, K. J. Berry, K. S. Murray, M. Irving, P. E. Clark, *Inorg. Chem.* **1984**, *23*, 283–300.

[6] E. B. Fleischer, A. M. Shachter, *Inorg. Chem.* **1991**, *30*, 3763–3769.

[7] X. Chi, A. J. Guerin, R. A. Haycock, C. A. Hunter, L. D. Sarson, *J. Chem. Soc. Chem. Commun.* **1995**, 2567–2569.

[8] a) K. Ogawa, Y. Kobuke, *Angew. Chem.* **2000**, *112*, 4236–4239; *Angew. Chem. Int. Ed.* **2000**, *39*, 4070–4073; b) K. Ogawa, T. Zhang, K. Yoshihara, Y. Kobuke, *J. Am. Chem. Soc.* **2002**, *124*, 22–23.

[9] E. Iengo, B. Milani, E. Zangrando, S. Geremia, E. Alessio, *Angew. Chem.* **2000**, *112*, 1138–1141; *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 1096–1099.

[10] S. Anderson, H. L. Anderson, A. Bashall, M. McPartlin, J. K. M. Sanders, *Angew. Chem.* **1995**, *107*, 1196–1200; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1096–1099.

[11] G. S. Wilson, H. L. Anderson, *Chem. Commun.* **1999**, 1539–1540.

[12] E. Iengo, E. Zangrando, R. Minatel, E. Alessio, *J. Am. Chem. Soc.* **2002**, *124*, 1003–1013.

[13] E. Alessio, M. Macchi, S. L. Heath, L. G. Marzilli, *Inorg. Chem.* **1997**, *36*, 5614–5623.

[14] The crystals of (**1 Zn**)$_2$, when redissolved in $CDCl_3$, yielded the same spectrum as before crystallization.

[15] Of the resonances of 4-pic, only the methyl signal (relatively broad peak at $\delta = 2.21$) could be attributed unambiguously; owing to the occurrence of dynamic processes involving coordination of 4-pic to the zinc porphyrins, the H2,6 and H3,5 resonances are very likely broadened beyond detection.

[16] a) SHELX-97, G. M. Sheldrick, *Programs for Crystal Structure Analysis,* University of Göttingen, **1998**; b) WinGX - A Windows Program for Crystal Structure Analysis. L .J. Farrugia, *J. Appl. Crystallogr.*, **1999**, *32*, 837–838; c) A. L. Speck, *Acta Crystallogr. Sect A* **1990**, *46*, C-34.

Received: June 27, 2002 [F4211]