A novel open-box shaped pentamer of vertically linked porphyrins that selectively recognizes S-bonded Me_2SO complexes

Enzo Alessio,*[a] Michela Macchi,[a] Sarah Heath[b] and Luigi G. Marzilli*[c]

[a] *Dipartimento di Scienze Chimiche, Università di Trieste, 34127 Trieste, Italy*
[b] *Department of Chemistry, University of Newcastle-Upon-Tyne, Newcastle, UK NE1 7RU*
[c] *Department of Chemistry, Emory University, Atlanta, Georgia 30322, USA*

The Zn derivative of a new stable open-box shaped pentamer of vertically linked porphyrins, formed quantitatively by treatment of tetrapyridylporphyrin with [Ru(TPP)CO], adds S-bonded Ru^{II}–Me_2SO complexes which can enter the box to form adducts containing the rare bridging Me_2SO.

The design of discrete, ordered arrays of porphyrins has attracted much recent interest, leading to synthetic methodologies with a 'building block' approach.[1] Mixed 4′-pyridyl/phenyl porphyrins (PyPs)† are particularly attractive linkers for metal centres since the pyridyl N position is fixed relative to the porphyrin ring. Depending on whether the metals sit in a coordination compound or in a porphyrin, very different ordered arrays can be constructed.[2–5] Such assemblies can have properties that are new or different from those of the constituents. For example, Anderson *et al.*[6] found that an array of five porphyrins with TPyP perpendicularly bound to a cyclic zinc porphyrin tetramer was photoactive while the separate constituents were not.

Coordination of the 4′-pyridyl groups of TPyP to [Ru(TPP)(CO)(EtOH)][7] afforded a pentamer, (TPyP)[Ru(TPP)(CO)]$_4$ **1**, with a predicted shape best described as two attached open-ended square boxes sharing a common bottom (TPyP) and with four Ru(TPP)(CO) as walls (Fig. 1). Assuming normal bond distances and angles,[8] we estimate a cavity width of *ca.* 20 Å at the base. This is the first five-porphyrin species with this shape that is perfectly stable in solution. In addition to the four Ru^{II} centres, the TPyP can host an additional metal ion. We describe here the zinc derivative [Zn(TPyP)][Ru(TPP)(CO)]$_4$ **1Zn**. We also synthesized two trimers with different geometries, (*trans*-DPyDP)[Ru(TPP)(CO)]$_2$ **2**[9] and (*cis*-DPyDP)[Ru(TPP)(CO)]$_2$ **3**, a dimer, [Ru(TPP)(CO)(MPyTP)] **4**, and the corresponding zinc derivatives of **3** (**3Zn**) and **4** (**4Zn**).

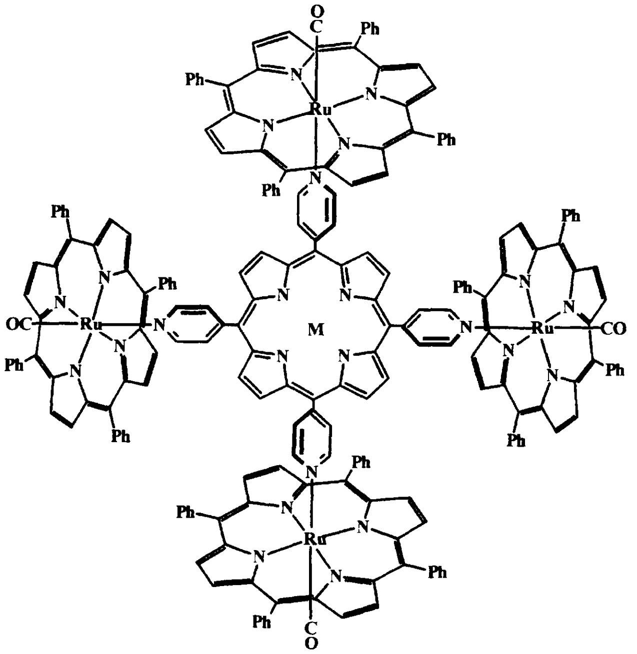

Fig. 1 Schematic drawing of pentamers **1** (M = 2 H^+) and **1Zn** (M = Zn^{2+})

All preparations were carried out in $CHCl_3$ at room temperature. [Ru(TPP)(CO)(EtOH)] added rapidly and quantitatively (assessed by ^1H NMR) to PyPs to afford products which precipitated in good yield after concentration of reaction solutions and addition of diethyl ether.‡ Only **2**, the least soluble oligomer, precipitated during the reaction. Interestingly, **1** is considerably more soluble in $CHCl_3$ than TPyP. All reactions were quite selective, and no further purification of the products was required. Zinc derivatives were best synthesized by treatment of **1**, **3** and **4** with an excess of zinc acetate in $CHCl_3$–MeOH. The visible spectrum of each oligomer was essentially the sum of those of each constituent porphyrin. ^1H NMR spectroscopy was a powerful tool for establishing the site of coordination of Ru(TPP)(CO) to PyPs. Pyridyl ^1H NMR signals were always sharp; no exchange between coordinated and free PyPs was observed. Signal integration revealed adduct stoichiometry, while the pyrrole resonances of PyP were characteristic of the geometry and allowed us to assess unambiguously a *cis* or *trans* substitution pattern. COSY spectra allowed unambiguous signal assignments. All PyP resonances were shifted upfield by the anisotropic [Ru(TPP)(CO)] units. The shielding effect was highest for the protons closest to ruthenium, decreasing gradually as the Ru–proton distance increased.[3,4,6] A cumulative shielding effect dependent on the number of bound [Ru(TPP)(CO)] units was also clearly evident. For example, each ruthenium–porphyrin unit shifted the NH resonance of PyPs *ca.* 0.5 ppm upfield.[6] The resonances of TPP protons were only very slightly affected by coordination of the pyridylporphyrin to ruthenium. The full NMR characterization of dimers, trimers and pentamers will be reported in a forthcoming paper. The presence of Zn inside PyPs did not affect significantly the chemical shifts of the adducts.

The high symmetry of the pentamer leads to a particularly simple NMR spectrum (Fig. 2). The high cumulative shielding effect of the four TPP rings perpendicular to the TPyP ring in **1** results in dramatic upfield shifts of the pyrrole and NH resonances (*ca.* 2 ppm *vs.* free TPyP).

Compared to the only other related porphyrin pentamer,[6] **1** is considerably more stable in solution and no sign of dissociation of the peripheral porphyrins from TPyP was observed, even in quite dilute solutions (0.3 mmol dm^{-3}). In **1**, although all sixteen phenyl rings are equivalent, the pairs of *o*- and *m*-protons of each ring are clearly nonequivalent; the signals of each pair are distinct multiplets. COSY connections between *o*- and *m*-H on each side of the ring (Fig. 2) can be attributed to hindered rotation about the *meso* carbon to phenyl carbon bond;[10] the phenyl rings are probably nearly perpendicular to the Ru–TPP mean plane, such as in [Ru(TPP)(CO)(py)][8] and

[Ru(TPP)(CO)(EtOH)].[10] The pyridyl rings should also be nearly perpendicular to the TPyP mean plane. Thus each box would have a rim around the opening and the bottom, restricting somewhat the two equivalent cavities.

The relatively open architecture of **1Zn** allows it to bind coordination compounds. We observed that **1Zn**, but not **1**, can interact with the oxygen atom of Me$_2$SO both free and S-bonded to a metal centre. Addition of an equimolar amount of **1Zn** to a CDCl$_3$ solution of an inert Ru–Me$_2$SO complex such as *cis,fac*-[RuCl$_2$(Me$_2$SO)$_3$(NH$_3$)] **5**[11] induced a 0.3 ppm upfield shift of the NH$_3$ signal and dramatic upfield shift and broadening of the three sharp Me$_2$*S*O peaks of **5** (3.44, 3.43 and 3.35 ppm); these signals were transformed into one broad signal at δ 2.81. The data also show that the equilibrium between **5** and **1Zn** is relatively fast on the NMR timescale. The upfield shift of *ca.* 0.5 ppm is comparable to the *ca.* 0.7 ppm for the ^{1}H NMR resonance of Me$_2$SO on addition of 1 equiv. of **1Zn**. The magnitude of these upfield shifts induced by **1Zn** indicates that, when Me$_2$SO enters the cavity of the pentamer and binds to zinc, the ligating atom is most likely oxygen.[12] Furthermore, the resonances of complexes without Me$_2$*S*O ligands, such as *trans,cis,cis*-[RuCl$_2$(CO)$_2$(py)$_2$], or with exclusively O-bonded Me$_2$SO, such as *cis,fac*-[RuCl$_2$(CO)$_3$(Me$_2$S*O*)],[13] were left unchanged by addition of **1Zn**. Thus, although the oxygen of coordinated Me$_2$*S*O is in a crowded environment in **5**, it appears to interact with **1Zn** nearly as well as the O of Me$_2$SO.

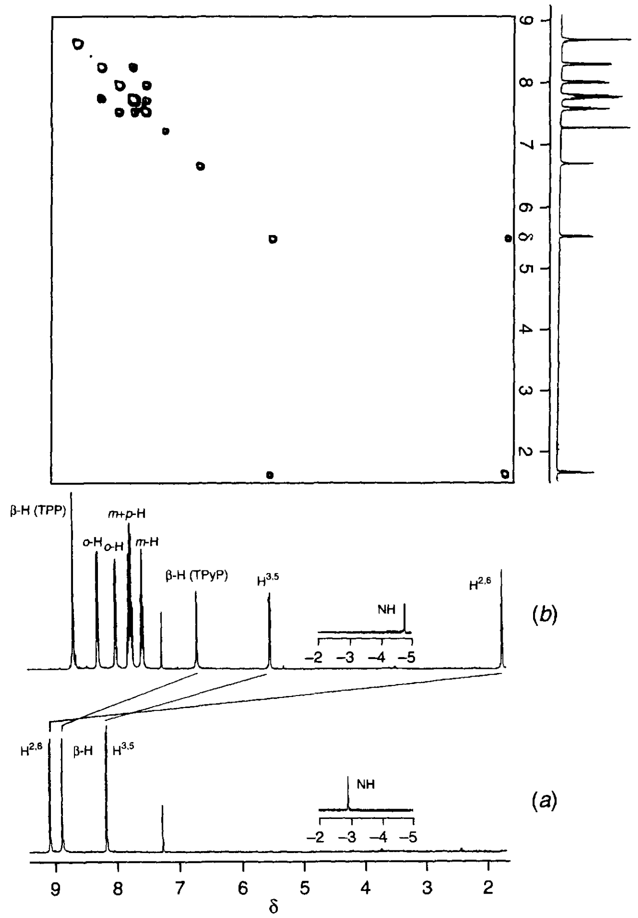

Fig. 2 Bottom: comparison of the ^{1}H NMR spectra (CDCl$_3$, 400 MHz) of TPyP (*a*) and **1** (*b*) with the differences in shift of TPyP signals induced by coordination to four Ru(TPP)(CO) units indicated. Top: COSY spectrum of **1**.

We also observed that the anisotropic effect of **1Zn** on the signals of Ru–Me$_2$*S*O complexes correlates with the basicity of the oxygen atom of Me$_2$*S*O. In fact, addition of 1 equiv. of **1Zn** to *cis*-[RuCl$_2$(Me$_2$SO)$_3$(CO)] **6**[13] induced only a minor upfield shift and a slight broadening of the Me$_2$SO resonances (δ 3.30, 3.15, 2.80 *vs.* δ 3.43, 3.25, 2.84 in **6**). Further replacement of an Me$_2$SO with a CO molecule, such as in *cis,cis,trans*-[RuCl$_2$(CO)$_2$(Me$_2$SO)$_2$] **7**, resulted in even smaller effects.

These results demonstrate that **1Zn** selectively recognizes S-bonded Me$_2$SO complexes through an interaction between the Zn ion inside the cavity and the oxygen atom of Me$_2$*S*O. Since there is no correlation between complex size and the magnitude of the effect, **1Zn** can be thought of as a probe for assessing the basicity of the oxygen atoms of Me$_2$*S*O ligands. Since the oxygen atom basicity is affected in turn by the donor/acceptor properties of the other ligands of the complex, this method could be used to assess the metal-donor ability of other types of ligands, such as nucleobases.

Interactions between the oxygen atom of S-bonded sulfoxide ligands and metal species are known for the solid state,[14] but this is the first unambiguous demonstration of such an interaction in solution.

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Footnotes

† *Abbreviations*: TPP = tetraphenylporphyrin; MPyTP = 5-pyridyl-10,15,20-triphenylporphyrin; *cis*-DPyDP = 5,10-dipyridyl-15,20-diphenylporphyrin; *trans*-DPyDP = 5,15-dipyridyl-10,20-diphenylporphyrin; TPyP = tetrapyridylporphyrin; Me$_2$*S*O = S-bonded Me$_2$SO; Me$_2$S*O* = O-bonded Me$_2$SO.

‡ A slight excess of [Ru(CO)(TPP)(EtOH)] over a 1 : 1 stoichiometry was used in all preparations. All products precipitated as non-crystalline solids (melting points > 340 °C) and gave satisfactory elemental analyses.

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