Octaethylporphyrinato Rhodium Cation Dimer, [(OEP)Rh]$_2^{+2}$: Strong Dimer Bonding resulting from Both Rhodium(II)–Rhodium(II) and Interporphyrin Cation Radical Interactions

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Octaethylporphyrinato rhodium cation, [(OEP)Rh]$^+$, forms a dimer, [(OEP)Rh]$_2^{+2}$, that is tightly bound through both a Rh^{II}–Rh^{II} bond and interporphyrin cation radical π–π interactions.

Octaethylporphyrinato rhodium(III) iodide, (OEP)Rh–I reacts with a stoichiometric quantity of Ag$^+$X$^-$(X$^-$ = BF$_4$, ClO$_4$, PF$_6$) in CH$_2$Cl$_2$, where each of the constituents is rigorously dehydrated, to form cation dimers, [(OEP)Rh]$_2^{+2}$ (2X$^-$) **1**. ^{1}H NMR and electronic spectra for **1** are shown in Figs. 1 and 2. Addition of pyridine to a CH$_2$Cl$_2$ solution of **1** results in cleavage of the dimer units to form a diamagnetic six-coordinate rhodium(III) pyridinate complex,[1] [(OEP)Rh(NC$_5$H$_5$)$_2$]$^+$X$^-$.†

Absence of temperature dependence for both the chemical shifts and line widths for the ^{1}H NMR of **1** (280–380 K) demonstrates that the cation dimer unit, [(OEP)Rh]$_2^{+2}$, is diamagnetic and not significantly dissociated up to 380 K. All of the ^{1}H NMR resonances of **1** (Fig. 1) [δ(–CH=) 4.70; δ(CH$_2$) 1.93, 1.51; δ(CH$_3$) 0.92] occur at exceptionally high field positions compared with diamagnetic metalloporphyrin dimers containing aromatic porphyrin units such as those in [(OEP)Rh]$_2$ [δ(–CH=) 9.14; δ(CH$_2$) 4.33, 3.98; δ(CH$_3$) 1.6] (Table 1). The ^{1}H NMR shift positions in **1** approach the values associated with a localized electronic structure and are a clear indication that the ring current shifts associated with aromatic porphyrins have been effectively quenched for **1**. Splitting of the electronic transitions in both the visible and Soret regions, and appearance of a low energy band (λ_{max} = 793 nm) in the electronic spectrum for **1** (Fig. 2) also indicate that the porphyrin π system has been substantially altered from that of a typical metalloporphyrin.

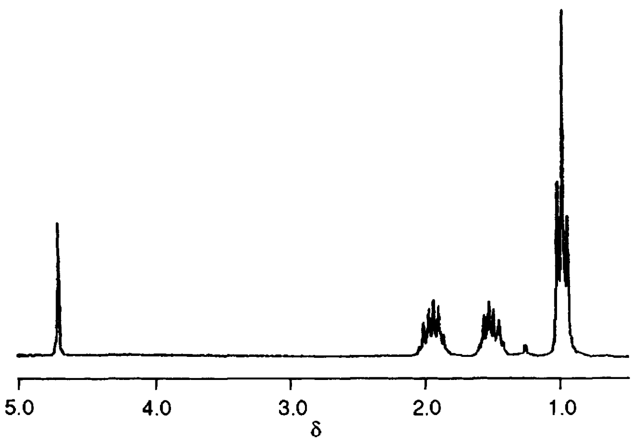

Fig 1 ^{1}H NMR spectrum of [(OEP)Rh]$_2^{+2}$ (2BF$_4^-$) in CD$_2$Cl$_2$ (2.75 × 10^{-3} mol dm^{-3}; 293 K) (δ(–CH=) 4.70; δ(CH$_2$) 1.93, 1.51; δ(CH$_3$) 0.92)

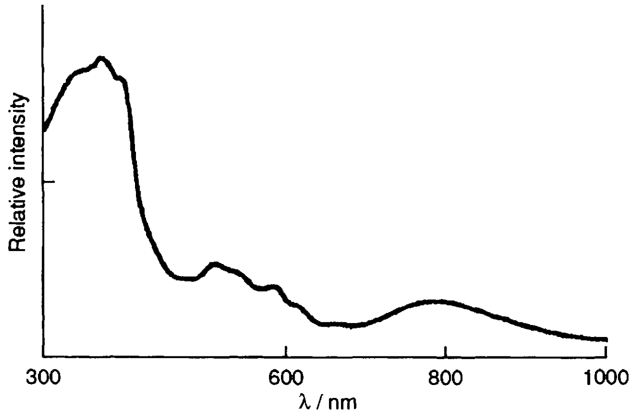

Fig. 2 Absorption spectra of [(OEP)Rh]$_2^{+2}$ (2BF$_4^-$) in CH$_2$Cl$_2$ (2.8 × 10^{-4} mol dm^{-3}; 293 K) (λ_{max} 341, 370, 394, 511, 585, 793 nm)

Cofacial metalloporphyrin dimers are known to result from either metal–metal bonding[2,3] or multicentered interporphyrin interactions in octaethylporphyrin cation radical derivatives.[4–7] [(OEP)Ru]$_2$ is a structurally characterized cofacial dimer that contains a Ru^{II}–Ru^{II}(d^6–d^6) double bond [(1σ + 1π); $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$], an S = 1 ground configuration ($\pi_X^{*1}\pi_Y^{*1}$), and aromatic porphyrin units.[8] [(OEP)Rh]$_2^{+2}$ has the same number of electrons as [(OEP)Ru]$_2$ and could potentially contain doubly bonded Rh^{III} (d^6) centres, but this formulation for [(OEP)Rh]$_2^{+2}$ is eliminated by the diamagnetism and loss of porphyrin aromaticity observed for **1**. [(OEP)Zn]$^+$ cation radical dimers **2** are prototypes for cofacial dimers where the porphyrin cation radical units are bonded together exclusively through interporphyrin π–π interactions.[6] Disruption of the π system for species of the type **2** are manifested by ^{1}H NMR shifts and electronic spectral features similar to those for **1**.[4] The distinctive low energy transition in the electronic spectrum of **2** (λ_{max} 920 nm)‡ was assigned to a transition between the bonding and antibonding orbitals that arise from the interporphyrin cation radical π–π interaction,[4] and this is most probably also the origin of the 793 nm band for **1**. Direct evidence for loss of porphyrin aromaticity in (OEP)Zn cation dimers is provided by structural characterization of [(OEP)Zn(H$_2$O)]$_2^{+2}$, which shows an alternation of bond lengths for the inner 16-membered porphyrin ring characteristic of a localized electronic structure.[6] Based on the ^{1}H NMR evidence for loss of porphyrin aromaticity and the distinctive features in the electronic spectrum of **1**, [(OEP)Rh]$_2^{+2}$ is formulated as the dimer of a porphyrin cation radical complex of rhodium(II). Rhodium(II) centres in porphyrin complexes have a (d$_{xy}$d$_{xz}$d$_{yz}$)^{6}d$_{z^2}^1$ ground configuration[9] and typically form Rh^{II}–Rh^{II}(d$_{z^2}$–d$_{z^2}$) σ bonds like that in [(OEP)Rh^{II}]$_2$, and the diamagnetism of **1** is consistent with the presence of a metal–metal bond. Absence of dissociation of **1** at conditions (380 K) where both **2** and [(OEP)Rh]$_2$ are extensively dissociated[2,4] indicates that the dimer bonding in **1** is stronger than in related complexes that contain either a π–π or a Rh–Rh bond. The monomer units in [(OEP)Rh]$_2^{+2}$ thus can be viewed as being firmly held together by an unusual type of multiple bond consisting of a Rh^{II}–Rh^{II} single bond and a delocalized interporphyrin cation radical bond.

Table 1 ^{1}H NMR shifts for (OEP)M complexes (CD$_2$Cl$_2$)

Complex	T/K	–CH=	–CH$_2$–	–CH$_3$
[(OEP)RH]$_2^{+2}$	293	4.70	1.93, 1.51	0.92
[(OEP)Zn]$_2^{+2}$	219	3.49	1.42	0.56
[(OEP)Rh]$_2$	293	9.14	4.33, 3.98	1.61
(OEP)RhI	293	10.31	4.18	1.98

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Footnotes

† ^{1}H NMR spectrum $\delta(C_5D_5N)$: 10.74(–CH=), 4.16(CH_2), 1.92(CH_3).

‡ Electronic spectrum of $[(OEP)Zn]^+$ cation radical dimer taken in MeOH–$CHCl_3$ (10 : 1) at −30 °C; Broad intense low energy transition centred at 920 nm (ref. 4).

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