

## Superimposed saddle and ruffled distortions of the porphyrin in iodo-(pyridine-*N*)(5,10,15,20-tetraphenylporphyrinato- $\kappa^4$ N)rhodium(III) toluene solvate

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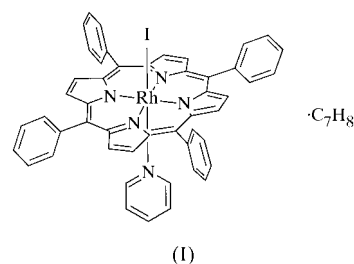
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In the title compound,  $[\text{Rh}(\text{C}_{44}\text{H}_{28}\text{N}_4)(\text{C}_5\text{H}_5\text{N})]\cdot\text{C}_7\text{H}_8$ , the porphyrin ring experiences significant distortion from planarity (a saddle conformation with a superimposed ruffling), as a result of steric interactions with the 2,6-H atoms of the axial pyridine ligand. This also leads to a slight lengthening of the Rh–pyridine bond [Rh–N 2.102 (7) Å] relative to those seen in other pyridine adducts of six-coordinate Rh<sup>III</sup>. The metric parameters of the porphyrin core are comparable with those of related metalloporphyrin derivatives. No significant intermolecular interactions are observed between the metalloporphyrin and disordered solvate species.

### Comment

While the molecular structures of several Co–porphyrin adducts with nitrogenous heterocyclic axial ligands have been determined, the Rh analogues remain crystallographically uncharacterized (Senge, 2000). Since the imidazole residue of histidine is a common axial ligand in heme-based proteins, metalloporphyrin complexes of this and related heterocycles, such as pyridine, pyrazole and their derivatives, are used extensively in biomimetic studies (Collman & Wang, 1999). Although, in bioinorganic chemistry, Co–porphyrins are by far the most popular group IX metalloporphyrin derivatives, the high affinity of Rh–porphyrin species for O<sub>2</sub> and the kinetic stability of the resulting adducts make the Rh analogues very interesting candidates for biomimetic work on respiratory chain enzymes, such as cytochrome *c* oxidase (Collman & Boulatov, 2000). The success of such studies relies on the ability of the synthetic chemist to construct a porphyrin ligand that provides a coordination environment similar to that at the

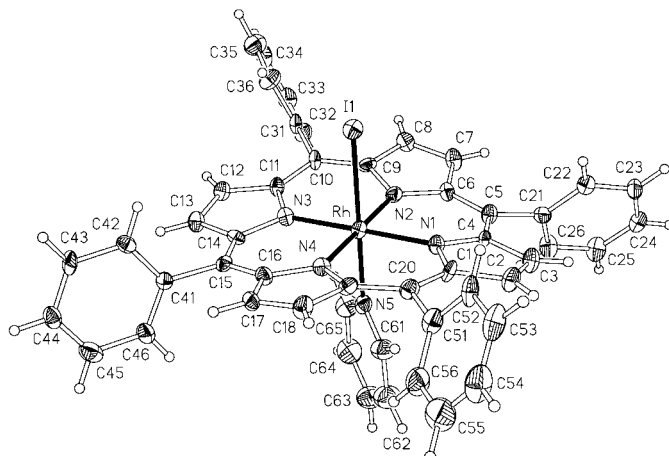
catalytic site of the enzyme under study. It thus becomes useful to know the type and degree of the distortion that a metalloporphyrin undergoes upon coordination of a heterocyclic base to the metal centre. Since, for synthetic reasons, derivatives of the *meso*-tetraphenylporphyrin dianion (TPP) are usually used in such biomimetic studies, we have chosen to investigate the molecular structure of the toluene solvate of the title  $[\text{Rh}(\text{TPP})\text{I}]$  adduct with pyridine, *i.e.*  $[\text{Rh}(\text{TPP})\text{I}(\text{py})]\cdot\text{C}_7\text{H}_8$ , (I). Another interesting issue that such studies can address is whether the significantly lower affinity of the Rh<sup>III</sup> centre in a porphyrin environment for pyridine compared with phosphines (Collman & Boulatov, 2000) correlates with the different degree of steric perturbation of the macrocycle in the corresponding adducts.



The molecular structure of (I) is shown in Fig. 1, and selected interatomic distances and angles are presented in Table 1. The most conspicuous feature of the structure is the significant distortion of the TPP core from planarity. The ‘ruffling’ of the core is superimposed on a ‘saddle’ deformation, resulting in a decrease in the overall symmetry of the core to C<sub>1</sub> (Fig. 2). As expected for a ruffled porphyrin, the *meso*-C atoms are displaced alternately above and below the least-squares plane of the 24-atom porphyrin core. The maximum displacement of an atom of the porphyrin core from its least-squares plane is 0.356 (8) Å (r.m.s. deviation 0.199 Å). This value is significantly larger than the maximum displacement observed in most other Rh–porphyrin derivatives containing either five- or six-coordinate Rh, for example, 0.18 Å in  $[\text{Rh}(\text{OEP})(m\text{-C}_6\text{H}_4\text{CN})]$  (OEP is the 2,3,7,8,12,13,17,18-octaethylporphyrin dianion; Zhou *et al.*, 1998) and 0.11 Å in  $[(\text{PhCH}_2\text{NC})\text{Rh}(\text{TPP})\{\text{C}(\text{NHCH}_2\text{Ph})_2\}]$  (Boschi *et al.*, 1989), but is appreciably smaller than the maximum displacement of 0.484 (4) Å observed in the highly distorted porphyrin core of  $[\text{Rh}(\text{TPP})(\text{CH}_2\text{Cl})]$  (Collman & Boulatov, 2001a). Ruffled cores have been observed in other metalloporphyrin–pyridine adducts, such as  $[\text{Co}(\text{TPP})\text{Cl}(\text{py})]$  (Sakurai *et al.*, 1975) and  $[\text{Co}(\text{TPP})(3,5\text{-lutidine})]$  (Scheidt & Ramanuja, 1975). The distortion of the macrocycle is a result of unfavourable steric interactions between the 2,6-H atoms of the aromatic six-membered cyclic ligand and the porphyrin core. Orientation of the pyridine plane relative to the *M*–N<sub>porphyrin</sub> vectors is also determined by the drive to decrease steric interactions. Thus, the N1–Rh–N5–C61 dihedral angle in (I) is 41.0 (7)°, with 45° representing the minimum steric interaction. Despite these structural changes, the closest H<sub>py</sub>⋯N<sub>porphyrin</sub> contact of 2.66 Å is still significantly shorter than the normal packing distance of 2.90 Å (Scheidt, 2000).

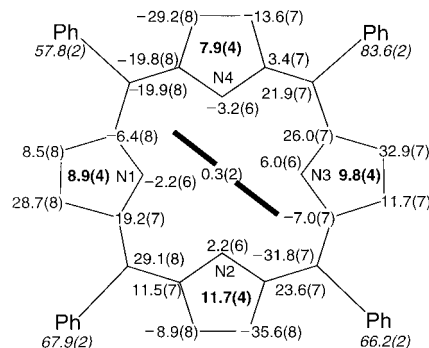
Interestingly, only the 'saddle' deformation of the macrocycle is observed in a structurally closely related complex, [Rh(TPP)(phenyl)], which possesses a closest  $H_{\text{ligand}} \cdots N_{\text{porphyrin}}$  contact of 2.74 Å, despite having the shorter Rh–axial-ligand distance [Rh–C of 1.985 (6) Å, *cf.* Rh– $N_{\text{py}}$  of 2.102 (7) Å in (I); Collman & Boulatov, 2001*b*]. This arises because of the substantial displacement of the Rh atom from the porphyrin plane towards the phenyl ligand. In contrast, Rh–porphyrin adducts with axial ligands bound through an  $sp^3$  donor atom, such as [Rh(OEP)Cl(PPh<sub>3</sub>)] (Thackray *et al.*, 1986) and [Rh(por)(NMe<sub>2</sub>H)<sub>2</sub>]<sup>+</sup> [por is TPP (Fleisher *et al.*, 1973) or etioporphyrin I (Hanson *et al.*, 1973)], manifest significantly more planar cores, as do organometallic derivatives with compact alkyls, such as [Rh(OEP)(CH<sub>3</sub>)] (Whang & Kim, 1991).

As a result of the ruffled core, two of the peripheral phenyl groups of (I) are tilted significantly towards the iodide. The Rh– $N_{\text{porphyrin}}$  bonds are quite similar and are comparable with those found in other Rh–porphyrin complexes (Scheidt, 2000). The plane of the pyridine ligand forms an angle of 88.7 (2)° with the least-squares plane of the porphyrin core, while the Rh–I vector is tilted at 4.0° to the latter. Among the crystallographically studied species containing the *trans* py–Rh–I unit, [Rh(dH)<sub>2</sub>I(py)] (dH is the dimethylglyoxime monoanion) is most closely related, both structurally and electronically, to (I). The rhodoxime derivative manifests a somewhat shorter Rh– $N_{\text{py}}$  bond length [2.079 (3) Å], but a slightly longer Rh–I bond [2.6423 (4) Å; Geremia *et al.*, 1994]. Other Rh<sup>III</sup>–py complexes with *trans* ligands which are comparable to iodide in their *trans* influence also demonstrate shorter Rh– $N_{\text{py}}$  bonds, *viz.* 2.046 (1) Å in [Rh(dH)<sub>2</sub>Cl(py)] (Geremia *et al.*, 1994), 2.083 (9) and 2.041 (9) Å in the *trans*  $N_{\text{py}}\text{–Rh–}N_{\text{py}}$  unit of *mer*-[Rh(py)<sub>3</sub>Cl<sub>2</sub>(CH<sub>2</sub>Cl)] (Bradd *et al.*, 1999), and 2.069 (2) Å in *trans*-[RhBr<sub>2</sub>(py)<sub>4</sub>] (Muir *et al.*, 1987). The lengthening of the Rh– $N_{\text{py}}$  bond in (I) is most likely due to steric destabilization from the porphyrin core. In contrast, the respective Rh–I bond is slightly shorter than such bonds in comparable Rh<sup>III</sup>–iodo complexes; for example,



**Figure 1**  
The structure of (I), showing the atomic labelling scheme and 40% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii and the toluene solvate molecule has been omitted.

bond lengths of 2.666 (8) and 2.659 (8) Å occur for the *trans* I–Rh–I unit in *mer*-[RhI<sub>3</sub>(py)(CO)(COMe)] (Adams *et al.*, 1988), and lengths of 2.685 (1) and 2.661 (1) Å occur in [Rh(9S3)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (9S3 is 1,4,7-trithiacyclononane; Kim *et al.*, 1995).



**Figure 2**  
The conformation of the porphyrin in (I), showing the displacements of the core atoms and of Rh from the 24-atom least-squares plane of the porphyrin core (in pm; negative values correspond to displacement towards the iodide ligand). Absolute values of the angles (°) between the pyrrole rings and the least-squares plane of the 24-atom porphyrin core are shown in bold, and absolute values of the angles (°) between the least-squares planes of the phenyl substituents and the 24-atom least-squares plane are shown in italics. The relative orientation of the pyridine ligand is depicted by bold lines.

Finally, no significant intermolecular interactions are observed in the crystal lattice of (I). The closest porphyrin–porphyrin contact occurs between the phenyl substituents and is longer than 3.5 Å. Because of the axial ligands, the closest Rh··Rh distance is longer than 8 Å, which precludes  $\pi$ – $\pi$  interactions.

## Experimental

[Rh(TPP)I] was synthesized as described previously by Collman & Boulatov (2000). Crystals of (I) suitable for crystallographic studies were obtained as the toluene solvate at room temperature by layering a toluene solution of [Rh(TPP)I] containing 5 equivalents of pyridine with 5 volumes of pentane under anhydrous conditions. NMR and UV–visible spectra were taken on UnityInova-500 and Hewlett–Packard 8453 spectrometers, respectively. Spectroscopic analysis: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz,  $\delta$ , p.p.m.): 9.00 (*s*,  $\beta$ -pyrrolic, 8H), 8.15 (*dt*,  $J = 7.9$  and 2.3 Hz, *o*-Ph, 4H), 8.06 (*d*,  $J = 7.9$  Hz, *o'*-Ph, 4H), 7.42 (*m*, *m*-Ph and *m'*-Ph, 8H), 7.34 (*m*, *p*-Ph, 4H), 7.12–6.98 (*m*, toluene, 5H), 4.78 (*tt*,  $J = 7.6$  and 1.7 Hz, *p*-py, 1H), 4.08 (*t*,  $J = 7.2$  Hz, *m*-py, 2H), 2.09 (*s*, CH<sub>3</sub>-toluene, 3H), 1.33 (*d*,  $J = 6.5$  Hz, *o*-py, 2H); UV–vis (toluene,  $\lambda_{\text{max}}$ , nm): 431, 541, 576.

## Crystal data

[RhI(C<sub>44</sub>H<sub>28</sub>N<sub>4</sub>)(C<sub>5</sub>H<sub>5</sub>N)]·C<sub>7</sub>H<sub>8</sub>  
 $M_r = 1013.75$   
 Monoclinic,  $P2_1/n$   
 $a = 13.3463$  (3) Å  
 $b = 23.4600$  (1) Å  
 $c = 14.5584$  (3) Å  
 $\beta = 100.560$  (1)°  
 $V = 4481.1$  (2) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.503$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 5069 reflections  
 $\theta = 1.43$ – $24.70$ °  
 $\mu = 1.115$  mm<sup>-1</sup>  
 $T = 173$  (1) K  
 Plate, brown–red  
 0.20 × 0.11 × 0.07 mm

## Data collection

Siemens SMART CCD area-detector diffractometer	20 724 measured reflections
$\omega$ scans	7556 independent reflections
Absorption correction: empirical [SADABS (Sheldrick, 1996) and XPREP in SHELXTL (Siemens, 1995a)]	4849 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.82$ , $T_{\max} = 0.97$	$R_{\text{int}} = 0.099$
	$\theta_{\max} = 24.70^\circ$
	$h = -15 \rightarrow 15$
	$k = -20 \rightarrow 27$
	$l = -17 \rightarrow 17$

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0107P)^2 + 27.4982P]$
$R(F) = 0.070$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.126$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.130$	$\Delta\rho_{\max} = 0.64 \text{ e } \text{\AA}^{-3}$
7556 reflections	$\Delta\rho_{\min} = -0.76 \text{ e } \text{\AA}^{-3}$
560 parameters	
H-atom parameters constrained	

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

I1—Rh	2.6335 (9)	Rh—N4	2.032 (6)
Rh—N3	2.022 (6)	Rh—N1	2.035 (6)
Rh—N2	2.032 (6)	Rh—N5	2.102 (7)
N3—Rh—N2	89.7 (2)	N4—Rh—N5	90.6 (2)
N3—Rh—N4	90.2 (2)	N1—Rh—N5	89.5 (3)
N2—Rh—N4	179.5 (3)	N3—Rh—I1	88.89 (18)
N3—Rh—N1	179.1 (3)	N2—Rh—I1	87.50 (18)
N2—Rh—N1	90.3 (3)	N4—Rh—I1	92.04 (18)
N4—Rh—N1	89.8 (2)	N1—Rh—I1	92.02 (18)
N3—Rh—N5	89.5 (3)	N5—Rh—I1	176.97 (19)
N2—Rh—N5	89.9 (3)		

The toluene solvate species in (I) is disordered about two independent inversion centres. Refinements with an overall  $U_{\text{iso}}$  and occupancy parameter assigned to each solvate species established half-occupancy at each site, leading to a total of four toluene molecules per unit cell. Because some atoms are nearly overlapped at each site, the geometry of the toluene solvate species was tightly restrained to standard values, and atomic displacement parameters of pairs of atoms were constrained to be equal (C84 and C86, C73 and C77, and C74 and C76). In addition, the proximity of the two solvate sites leads to correlated occupancy of the sites. Representing the two solvate sites as *A* and *B*, and their centrosymmetrically related mates as *A'* and *B'*, leads to the spatial arrangement  $A'A \cdots BB'$  where species *A* and *B* are unacceptably close. Thus, the pairs  $A'B$  and  $AB'$  are stochastically dispersed throughout the crystal. H atoms were included at their calculated positions ( $C-H = 0.93$  and  $0.96 \text{ \AA}$ ) and in least-squares refinements were allowed to ride with an equivalent isotropic atomic displacement parameter 1.2 times (1.5 times for methyl-H atoms) that of the C atom to which they were attached.

Data collection: SMART (Siemens, 1995b); cell refinement: SMART; data reduction: SAINT (Siemens, 1995b); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Siemens, 1995a); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1606). Services for accessing these data are described at the back of the journal.

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