

## Influence of chloroform on crystalline products yielded in reactions of 5,10,15,20-tetraphenylporphyrin with HCl and copper(II) salts

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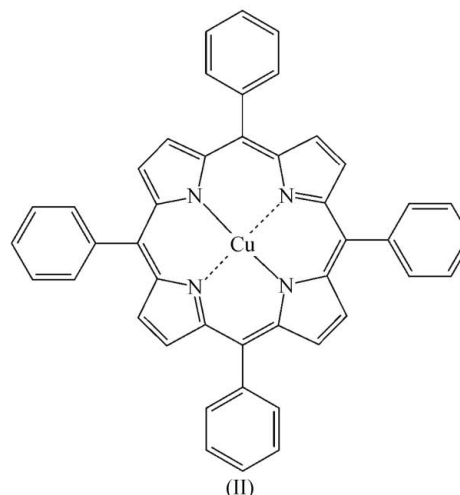
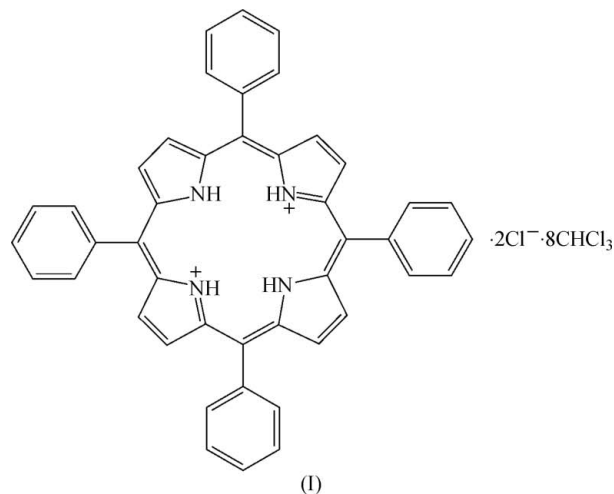
Chloroform was found to occupy the lattice of the protonated porphyrin and to promote crystallization of a different polymorphic form of a metalloporphyrin. The structure of 5,10,15,20-tetraphenylporphyrin-21,23-dium dichloride chloroform octasolvate,  $C_{44}H_{32}N_4^{2+} \cdot 2Cl^- \cdot 8CHCl_3$ , (I), in the solid state is described and compared with related solvates. The porphyrin macrocycle displays a distorted saddle shape, with chloride anions above and below the ring. Seven chloroform molecules are bound *via* C—H...Cl hydrogen bonds, while the link with the eighth solvent molecule is weaker. A new monoclinic polymorph of (5,10,15,20-tetraphenylporphyrinato)copper(II),  $[Cu(C_{44}H_{28}N_4)]$ , (II), crystallized from chloroform, is also presented.

### Comment

Porphyrins and metalloporphyrins have been studied for many years because of their biochemical relevance as well as their applications. In biology, these tetrapyrrolic macrocycles fulfil such diverse roles as molecular binding, light harvesting, catalysis, and energy and/or electron transfer (Burrell *et al.*, 2001). From the technological point of view, porphyrins have been useful in a range of applications, from molecular sensing to the development of dye-sensitized solar cells (Hagfeldt *et al.*, 2010). Also, these compounds have been found to possess a rich macromolecular chemistry, *i.e.* promoting DNA cleavage (Börjesson *et al.*, 2010), serving as the core for metallo-dendrimers (Newkome *et al.*, 1999) or as the building blocks for other self-organized nanostructures (Harada & Kojima, 2005).

Much work has been devoted to 5,10,15,20-tetraphenylporphyrin and its derived metal complexes, which is understandable given the facile and rapid synthesis of this porphyrin. On some occasions, protonated porphyrins may be obtained in parallel with metal complexes. While they do not share the popularity of their free-base or coordinated rela-

tives, porphyrin dications have been found very useful in elucidating the nature of the structural distortions of porphyrin derivatives.



The study of the geometrical distortion of porphyrins may give rise to interesting nanostructured materials. For instance, it has recently been demonstrated that the puckering of saddle-distorted porphyrins results in nanochannel materials in which photochemically induced electron transfer to guest molecules can be detected (Kojima *et al.*, 2007; Nakanishi *et al.*, 2008).

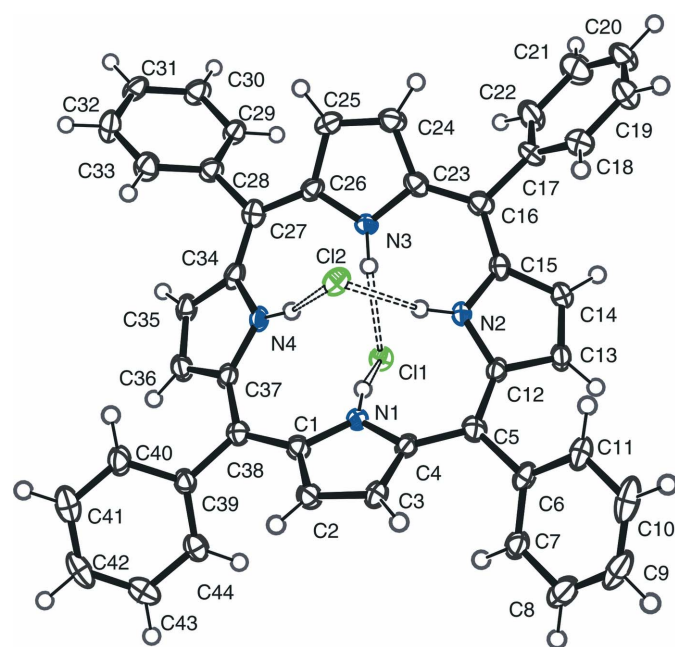
Porphyrin molecules upon protonation become nonplanar largely because of the strain caused by the four-H-atom interaction at the ring core (Stone & Fleischer, 1968). This behaviour is observed in several structures of protonated porphyrins, where the ring is forced to adopt a distorted geometry described as saddled (*sad*), ruffled (*ruf*), domed (*dom*), propeller-shaped (*pro*) or waved (*wav*). Saddled is the most common (Senge & Kalisch, 1999). Data on selected structures of protonated porphyrins are presented in Table 1. The symmetry of the porphyrin macrocycle deformation was analysed by Stone & Fleischer (1968) in terms of irreducible representations of the point group  $D_{4h}$ . The distortions can be classified as: *sad*  $B_{1u}$ , *ruf*  $B_{2u}$ , *dom*  $A_{2u}$ , *pro*  $A_{1u}$  and *wav*(1) or *wav*(2)  $E_g$ , respectively. From the symbols one can infer that

the local symmetry of the porphyrin molecule can be 2 or  $\bar{4}$  for the first two conformations. Local symmetry 4 is allowed only for *dom* and *pro*, whereas  $\bar{1}$  is allowed only for the *wav* forms. Obviously, this is true only for porphyrins with full  $D_{4h}$  symmetry. For an analysis of deformations in a less symmetric molecule, see Sun *et al.* (2012).

Generally, the presence of substituents on the  $\beta$  positions causes the porphyrins to deviate more from planarity than with *meso* (*i.e.* 5,10,15,20-) substituents. Cheng *et al.* (1997) compared *meso* (Ph, mesityl and H) and  $\beta$  (Et, H) substitution in several diacid porphyrins. Their octaethyl  $\beta$ -substituted porphyrins were less distorted than Ph- or mesityl-substituted molecules in *meso* positions. They concluded that the stiffness of the substituent must also be taken into account as a factor influencing the distortion. Among the compounds in Table 1, the  $\beta$  substitution by stiff Ph groups inevitably leads to a strongly distorted conformation ( $\Delta_{24} > 0.6$  and dihedral angles between the opposite pyrrole rings close to  $90^\circ$ ). In the present study, we investigated two new derivatives of *meso*-tetraphenylporphyrin.

In 5,10,15,20-tetraphenylporphyrin-21,23-diium dichloride chloroform octasolvate, (I) (Fig. 1), two N–H bonds (from N1 and N3) are directed above the mean plane of the molecule and form hydrogen bonds with chloride ion Cl1 and the remaining N–H bonds point down to the second chloride ion (Cl2) (see also Table 2).

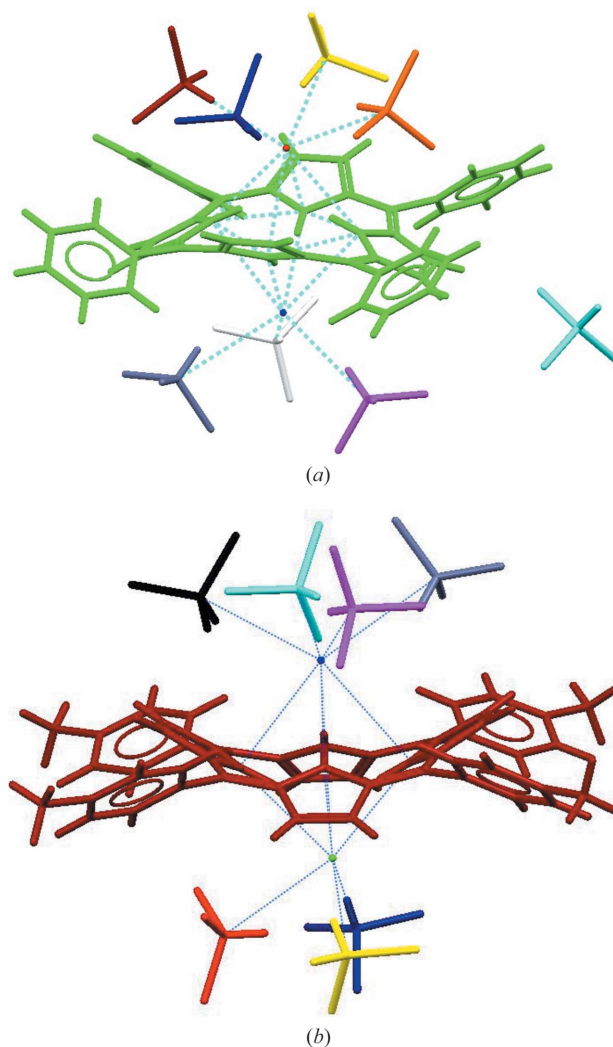
Three chloroform molecules bound by a C–H...Cl hydrogen bond to the Cl1 atom, as well as the stand-alone molecule, are well ordered. However, the remaining four chloroform molecules, all linked to the Cl2 atom, display strong disorder (see Fig. 2a). As the disordered chloroform



**Figure 1**

The molecular structure of 5,10,15,20-tetraphenylporphyrin-21,23-diium dichloride chloroform octasolvate, (I). The chloroform solvent molecules have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

molecules have a severe impact on the *R* indices, building an appropriate disorder model was crucial. In our attempt, all the chloroform molecules were restrained to the geometry of a ‘regular’ molecule. In order to define this, the Cambridge Structural Database (CSD; Allen, 2002) was queried for data on the mean chloroform geometry observed in crystals. A total of 4707 examples were found. These provided a statistically relevant estimation of the mean C–Cl bond length value (1.737 Å, with a sample standard uncertainty of 0.06 Å) and the mean 1,3 Cl...Cl distance (2.838 Å, with a sample standard uncertainty of 0.08 Å). All the disordered molecules were restrained to the above-mentioned values, while their standard uncertainties were shrunk to 0.02 Å. One molecule (C45–Cl3–Cl4–Cl5) had to be split over three positions, and the other three molecules were disordered over two positions. It appears all four molecules have some degree of ‘orbiting rotational freedom’ over the acceptor atom and may interchange, while still being linked to chloride atom Cl2.



**Figure 2**

A view of the hydrogen bonding of the chloroform solvent molecules to the chloride anions in (a) 5,10,15,20-tetraphenylporphyrin-21,23-diium dichloride chloroform octasolvate, (I), and (b) 5,10,15,20-tetrakis(4-methylphenyl)porphyrin-21,23-diium dichloride chloroform heptasolvate (Grubisha *et al.*, 2008).

Many similarities can be found in the structure of 5,10,15,20-tetrakis(4-methylphenyl)porphyrin-21,23-dium dichloride chloroform heptasolvate (Grubisha *et al.*, 2008). Again, the porphyrin ring is distorted, which manifests itself in dihedral angles of *ca* 120° between opposite pyrrole rings. More interestingly, the chloroform solvent molecules are bound to the chloride ions by C–H···Cl hydrogen bonds, four from one side of the porphyrin ring plane and three from the other (Fig. 2*b*), forming a similar pattern to that of (I).

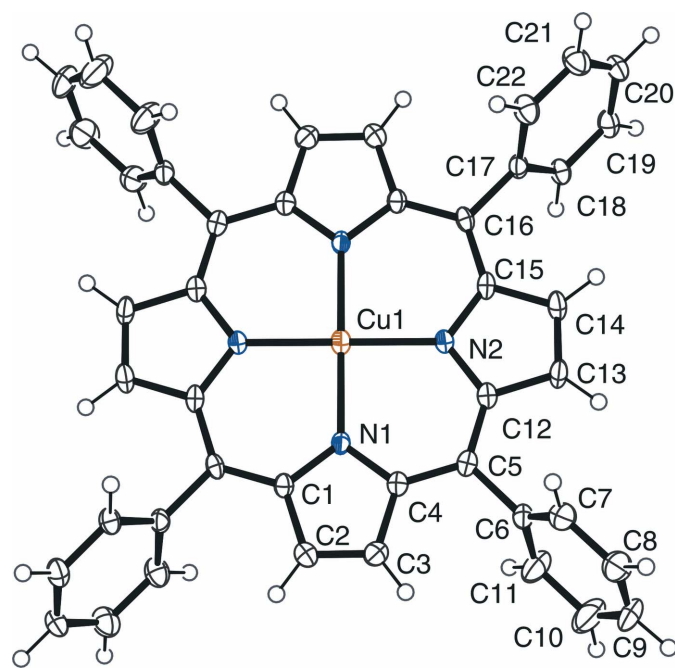
*meso*-Tetraphenylporphyrindium dichloride is known to form ‘binary’ solvates with acetonitrile and water (Larsen *et al.*, 2004). It forms a similar core with a saddle-distorted porphyrin and Cl<sup>−</sup> anions as acceptors of the N–H bonds from both sides of the porphyrin plane. The similarity ends there as the structure is further stabilized by O–H···Cl hydrogen bonds with water molecules and the remaining two acetonitrile molecules seem to play a space-filling role only.

Other structures with 22,24-dihydro-5,10,15,20-tetraphenylporphyrindium dications contain a number of combinations of anions and solvents: porphyrin bis(hydrogen sulfate) methanol disolvate (Senge & Kalisch, 1999), porphyrin diperchlorate benzene monosolvate (Cheng *et al.*, 1997), porphyrin bis(tetrafluoroborate) chloroform monosolvate dihydrate (Rayati *et al.*, 2008) and porphyrin diperchlorate methanol monosolvate (Senge *et al.*, 1994; Senge & Kalisch, 1999).

In the case of 22,24-dihydro-5,10,15,20-tetraphenylporphyrin chloride ferrichloride, no solvent is trapped in the structure (Stone & Fleischer, 1968).

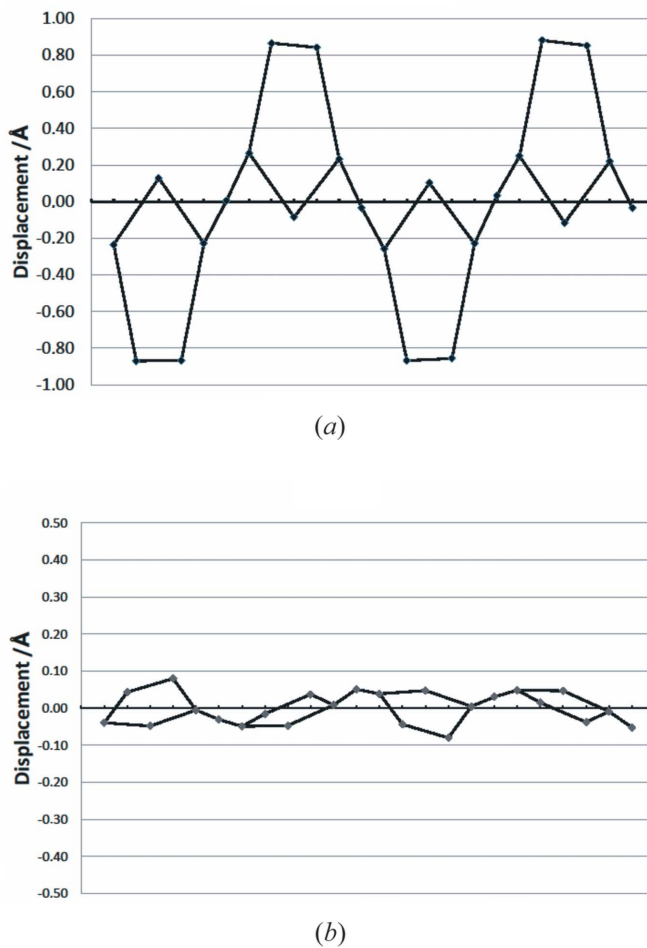
Two X-ray crystal structures for (5,10,15,20-tetraphenylporphyrinato)copper(II) (CuTPP), (II), have been deter-

mined so far, *viz.* a tetragonal form crystallizing in  $\bar{I}42d$ , determined twice [by Fleischer *et al.* (1964) at 295 K,  $d = 1.421 \text{ Mg m}^{-3}$ , then by Zeller *et al.* (2004) at 100 K,  $d = 1.461 \text{ Mg m}^{-3}$ ], and another tetragonal form with symmetry  $I4/m$  [He (2007),  $d = 1.290 \text{ Mg m}^{-3}$  at 290 K]. Other structures of CuTPP contain additional guest molecules, *e.g.* benzene and C<sub>78</sub> fullerene (Schwiertz *et al.*, 2009), 4-picoline (Byrn *et al.*, 1993) or *m*-xylene (Byrn *et al.*, 1991), C<sub>60</sub> fullerene either alone or accompanied by toluene and C<sub>2</sub>HCl<sub>3</sub> (Konarev *et al.*, 2001). While the conformation of the 24-membered macrocycle is saddled (local  $\bar{4}$  symmetry) for CuTPP crystallizing in  $\bar{I}42d$ , a flat core (local  $4/m$  symmetry) is observed in the case of the  $I4/m$  space group. The present monoclinic structure of (II) ( $P2_1/n$ ) (Fig. 3) has local  $\bar{1}$  symmetry which only allows for the wave conformation ( $E_g$ -type representation). The deviation of the macrocycle from flatness is not strong ( $\Delta_{24} = 0.0428 \text{ \AA}$ ), but clearly no fourfold symmetry is present (see Fig. 4). The same type of conformation with a local centre of inversion is present in all the solvated structures mentioned above (excluding Konarev *et al.*, 2001). Comparing the densities of the known polymorphs with that of (II) ( $1.394 \text{ Mg m}^{-3}$ ), we



**Figure 3**

The molecular structure of CuTPP, (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 4**

The linear display of the deviations of the 24 atoms of the macrocycle from their mean plane for (a) 5,10,15,20-tetraphenylporphyrin-21,23-dium dichloride chloroform octasolvate, (I), and (b) CuTPP (the horizontal axis is not to scale), (II).

see that when CuTPP crystallizes from chloroform it does not present the most dense packing and probably it is not the most thermodynamically stable. It follows the Ostwald's rule of stages (Ostwald, 1897; Threlfall, 2003), which states that crystallization often favours the least stable polymorphs. Although the validity of this rule is questionable, the balance between kinetics and thermodynamics allows us to obtain the less dense monoclinic form of CuTPP. Chloroform is generally disregarded as a solvent, because of its tendency to form disordered structures. However, it is worth keeping in mind that chloroform may be helpful when trying to obtain less stable polymorphs, as in the current case.

## Experimental

*meso*-Tetraphenylporphyrin [H<sub>2</sub>(TPP)] was synthesized according to the extensively used method devised by Adler *et al.* (1967). Chloroform was dried over molecular sieves while methanol was dried over metallic Mg. Both solvents were distilled prior to use.

H<sub>2</sub>(TPP) (120 mg, 0.2 mmol) was dissolved in chloroform (8 ml). Then, a 2 M solution of HCl (0.5 ml) was added to methanol (2.5 ml) and poured into the porphyrin solution. The resulting green solution was stirred for 10 min and then left to crystallize slowly at 263 K. After a few days, a small quantity of [H<sub>4</sub>(TPP)]Cl<sub>2</sub>·8CHCl<sub>3</sub> single crystals, suitable for X-ray analysis, appeared on the bottom of the flask. This deep-blue product was extremely unstable at room temperature, redissolving after some minutes if left in the solution and becoming very brittle while turning completely opaque when dried, at which point no reflections could be taken with the diffractometer (we suspect this was caused by the loss of the most volatile chloroform molecules). Therefore, extreme caution had to be observed in order to pick a fresh and appropriate crystal.

(5,10,15,20-Tetraphenylporphyrinato)copper(II) (CuTPP), (II), was synthesized by refluxing CuCl<sub>2</sub>·2H<sub>2</sub>O (234 mg) in dimethylformamide (50 ml) in the presence of H<sub>2</sub>(TPP) (425 mg) over a period of 2.5 h. The product was completely dried, washed twice with water and purified by chromatography on an alumina column, using chloroform as the eluent. The resulting red phase containing CuTPP was left open to the atmosphere at room temperature. After a few days, the chloroform had evaporated, leaving well formed crystals of (II).

## Compound (I)

### Crystal data

C <sub>44</sub> H <sub>32</sub> N <sub>4</sub> <sup>2+</sup> ·2Cl <sup>-</sup> ·8CHCl <sub>3</sub>	$\gamma = 76.356$ (2)°
$M_r = 1642.58$	$V = 3452.31$ (15) Å <sup>3</sup>
Triclinic, $P\bar{1}$	$Z = 2$
$a = 11.6031$ (3) Å	Mo $K\alpha$ radiation
$b = 12.6132$ (3) Å	$\mu = 1.06$ mm <sup>-1</sup>
$c = 24.5118$ (6) Å	$T = 120$ K
$\alpha = 87.706$ (2)°	$0.49 \times 0.40 \times 0.22$ mm
$\beta = 82.025$ (2)°	

### Data collection

Oxford Diffraction Xcalibur Sapphire2 (large Be window) diffractometer	derived by Clark & Reid (1995)
Absorption correction: analytical [CrysAlis PRO (Oxford Diffraction, 2006), a multifaceted crystal model based on expressions]	$T_{\min} = 0.705$ , $T_{\max} = 0.823$
	22549 measured reflections
	12824 independent reflections
	9236 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.030$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.095$	55 restraints
$wR(F^2) = 0.261$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\text{max}} = 3.32$ e Å <sup>-3</sup>
12824 reflections	$\Delta\rho_{\text{min}} = -2.09$ e Å <sup>-3</sup>
720 parameters	

## Compound (II)

### Crystal data

[Cu(C <sub>44</sub> H <sub>28</sub> N <sub>4</sub> )]	$V = 1611.4$ (2) Å <sup>3</sup>
$M_r = 676.24$	$Z = 2$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 14.5813$ (12) Å	$\mu = 0.72$ mm <sup>-1</sup>
$b = 8.6068$ (5) Å	$T = 120$ K
$c = 14.6191$ (11) Å	$0.53 \times 0.23 \times 0.02$ mm
$\beta = 118.56$ (1)°	

### Data collection

Oxford Diffraction Xcalibur Sapphire2 (large Be window) diffractometer	derived by Clark & Reid (1995)
Absorption correction: analytical [CrysAlis PRO (Oxford Diffraction, 2006), a multifaceted crystal model based on expressions]	$T_{\min} = 0.777$ , $T_{\max} = 0.992$
	11911 measured reflections
	3167 independent reflections
	2288 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.052$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$	223 parameters
$wR(F^2) = 0.147$	H-atom parameters constrained
$S = 0.96$	$\Delta\rho_{\text{max}} = 0.63$ e Å <sup>-3</sup>
3167 reflections	$\Delta\rho_{\text{min}} = -0.48$ e Å <sup>-3</sup>

All C- and N-bound H atoms were refined in isotropic approximation as riding on their parent atoms, with aromatic C—H = 0.95 Å, methine C—H = 1.00 Å and N—H = 0.88 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$ . The disorder in four of the eight chloroform molecules in (I) required a rather complex model. The solvent molecule containing atom C46 was ordered, but refined using isotropic Cl atoms. The three chloroform molecules containing atoms C47, C48 and C49, respectively, were fully ordered and were refined with anisotropic displacement parameters for the non-H atoms. The chloroform molecule containing atom C45 was refined as being disordered over three positions. The anisotropic displacement parameters of each disordered position for atom C45 were constrained to be equal, while isotropic displacement parameters were refined for the Cl atoms in all three orientations and constrained to be equal in one orientation. A SUMP restraint (Sheldrick, 2008) in the form of  $\text{sof}(1) + \text{sof}(2) + \text{sof}(3) = 1.000$  (1) was applied and gave a final distribution of the parts as 0.734 (6)/0.191 (5)/0.077 (4). Notably, the omission of the third orientation of this chloroform molecule results in a substantial increase of the  $R1$  index by *ca* 0.7%. The three solvent molecules containing atoms C50, C51 and C52 were found to be disordered and were refined as being split over two orientations with final occupation-factor ratios of 0.529 (19):0.471 (19), 0.904 (4):0.096 (4) and 0.587 (14):0.413 (14), respectively. Isotropic displacement parameters were refined for all non-H atoms of these solvent molecules, except for those of the Cl atoms of the minor orientation of the molecule containing atom C51, which were kept fixed at 0.04 Å<sup>2</sup>. In addition, the isotropic displacement parameters of the two disordered C-atom positions of each of these solvent molecules were constrained to be equal. The C—Cl and Cl...Cl distances in all of the disordered chloroform molecules were restrained to 1.737 (2) and 2.848 (2) Å, respectively, as described in the *Comment*. Despite the



**Table 1**

Dihedral angles ( $^{\circ}$ ) between the least-squares planes of opposite pyrrole rings and the average deviation of the 24-membered macrocycle from the least-squares plane,  $\Delta_{24}$  ( $\text{\AA}$ ) (Senge & Kalisch, 1999), in different protonated porphyrin dichlorides or other salts of protonated meso-tetraphenylporphyrins [programs used: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2006)].

Note that usually programs calculate acute dihedral angles, so the values cited here are those of the corresponding supplementary ones.

Anion	Solvent	py1–py3	py2–py4	$\Delta_{24}$	Substitution		Local symmetry
					meso	$\beta$	
Cl <sup>d</sup>	CHCl <sub>3</sub>	125.5 (4)	126.3 (4)	0.390	Ph	H	1
Cl <sup>b</sup>	CHCl <sub>3</sub>	120.32	121.88	0.429	4-MePh	H	1
Cl <sup>c</sup>	H <sub>2</sub> O/MeCN	126.4	111.6	0.446	Ph	H	1
Cl <sup>d</sup>	MeCN/hydro-quinone	90.69	90.69	0.64	Ph	Ph	2
Cl <sup>e</sup>	CH <sub>2</sub> Cl <sub>2</sub>	98.93	98.23	0.605	Ph	Et	1
Cl <sup>f</sup>	Toluene	103.5	103.5	0.556	Ph	Et	$\bar{4}$
Cl <sup>g</sup>	CHCl <sub>3</sub> /MeOH	131.34	134.29	0.376	Ph	Et, H <sup>†</sup>	1
Cl <sup>h</sup>	TTF/MeCN, H <sub>2</sub> O	94.13	94.13	0.617	Ph	Ph	2
Cl <sup>i</sup>	MeCN	90.35	90.35	0.647	Ph	Ph	2
Cl <sup>j</sup>	MeCN/CHCl <sub>3</sub> , H <sub>2</sub> O	90.6	90.6	0.639	Ph	Ph	2
Cl <sup>k</sup>	<i>p</i> -xylene/MeCN	90.05	90.05	0.644	Ph	Ph	2
Cl, FeCl <sub>4</sub> <sup>l</sup>	none	113.91	113.91	0.524	Ph	H	$\bar{4}$
Cl <sup>j</sup>	H <sub>2</sub> O	126.91	126.1	0.394	4-py	H	1
Cl <sup>k</sup>	<sup>t</sup> Bu–O–Me	115.86	115.86	0.496	4-MeO-COPh	<i>c</i> -Hexane	$\bar{4}$
BF <sub>4</sub> <sup>l</sup>	CHCl <sub>3</sub> /H <sub>2</sub> O	131.48	135.06	0.340	Ph	H	1
ClO <sub>4</sub> <sup>m</sup>	MeOH	118.56	117.26	0.464	H	Me, Et	1

<sup>†</sup> This structure presents a special feature, *i.e.* it contains three fused porphyrin rings. References: (a) this work; (b) Grubisha *et al.* (2008); (c) Larsen *et al.* (2004); (d) Harada & Kojima (2005); (e) Senge & Kalisch (1999); (f) Hu *et al.* (2007); (g) Jaquinod *et al.* (1998); (h) Nakanishi *et al.* (2008); (i) Kojima *et al.* (2007); (j) Stone & Fleischer (1968); (k) Finikova *et al.* (2002); (l) Rayati *et al.* (2008); (m) Senge *et al.* (1994).

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^{\circ}$ ) for (I).

D–H...A	D–H	H...A	D...A	D–H...A
N1–H1...Cl1	0.88	2.30	3.110 (5)	152
N3–H3A...Cl1	0.88	2.38	3.183 (6)	152
N2–H2A...Cl2	0.88	2.38	3.167 (5)	148
N4–H4...Cl2	0.88	2.40	3.198 (6)	152
C45–H45...Cl2	1.00	2.64	3.382 (10)	132
C46–H46...Cl1	1.00	2.50	3.474 (9)	166
C48–H48...Cl1	1.00	2.39	3.362 (8)	164
C49–H49...Cl1	1.00	2.63	3.492 (8)	145
C50–H50...Cl2	1.00	2.65	3.47 (2)	140
C51–H51...Cl2	1.00	2.52	3.467 (10)	158
C52–H52...Cl2	1.00	2.70	3.57 (2)	146

complex disorder model, the residual electron density (located in the disordered solvent region) is still high, indicating that the real structure is perhaps even more complex. This may be the main reason for the relatively large value of *R*<sub>1</sub>.

For both compounds, data collection: *CrysAlis PRO* (Oxford Diffraction, 2006); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2006);

software used to prepare material for publication: *WinGX* (Farrugia, 1999), *publCIF* (Westrip, 2010) and *PLATON* (Spek, 2009).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3092). Services for accessing these data are described at the back of the journal.

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