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Saddle-shaped macrocycle distortion and symmetry decrease in cobalt (II) *meso*-tetraphenylporphyrin: Structure of a dichloromethane solvate and DFT calculations



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HIGHLIGHTS

- Synthesis and crystal structure of new dichloromethane solvate form of cobalt (II) *meso*-tetraphenylporphyrin (CoTPP).
- First observation of a CoTPP structure with a saddle-shaped conformation.
- Potential energy surface calculation of torsion angle describing phenyl conformation in both non-solvated and solvate forms.
- Saddle-shaped macrocycle distortion dependence of the unlike phenyl conformation decreasing symmetry in the solvate.

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G R A P H I C A L A B S T R A C T



ABSTRACT

Many studies about porphyrins have emerged in recent years, including studies using porphyrins as building blocks for supramolecular assemblies. Understanding new solid state forms of porphyrins and the elucidation of their structures can have remarkable benefits for nanoscience and synthetic biology. In this study, a new pseudopolymorph of cobalt (II) meso-tetraphenylporphyrin, (CoTPP), was synthesized in a known one-pot reaction, rather than using many-step conventional methods, was isolated and was characterized for the first time by low-temperature single crystal X-ray diffraction. It is a nonstoichiometric solvate assembled into dichloromethane channels. The most striking feature of this structure is the conformation adopted by the porphyrin macrocycle. In contrast to the non-solvated form of CoTPP that exhibits a ruffled core distortion and crystallizes in the tetragonal space group I-42d, this solvated form has been crystallized in the triclinic space group Pi and shows a distinct saddle-shaped macrocycle distortion. In the triclinic form, the conformation of one of the four phenyl rings is remarkably different from the others. A potential energy surface scan of the torsional angles around the bonds between this phenyl moiety and the macrocycle of CoTPP in both the non-solvated and the solvate forms demonstrates that the saddle-shaped macrocycle distortion depends on the unusual phenyl conformation. The distortion is responsible for the symmetry decrease in the channel solvate form, causing a loss of the 4-fold rotoinversion axis observed in the non-solvated tetragonal phase, which has identical phenyl conformations. © 2014 Published by Elsevier B.V.

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Introduction

Over the last few decades, much attention has been given to multiporphyrin systems because they are able to modify or produce optical-electronic properties that are not observed in single porphyrins. The synthesis and characterization of a macrocycle as an individual molecule and its crystal packing modes can provide essential information for crystal engineering of multiporphyrin assemblies [1].

Among other properties, porphyrins exhibit an intense absorption band in the UV region (Soret band, 400–450 nm), as well as less intense bands in the visible region (Q bands, 500–650 nm), that are beneficial for the development of photosynthetic systems and molecular photonic devices [2]. In addition, a striking and important feature of these compounds is their ability to form channels and nano-sized cavities that can accommodate a wide range of ligands and solvate molecules. The use of porphyrins as clathrate "hosts" has the potential for application to many different chemical processes, including separation, sorption, catalysis, and drug delivery, as well as research into new or adaptive synthetic delivery routes, and is a promising field [3,4].

During our studies on the synthesis and characterization of porphyrin systems, we have identified a new solvate form of cobalt (II) *meso*-tetraphenylporphyrin (CoTPP) as a dichloromethane solvate. Unlike conventional synthesis methods, which typically require many steps, CoTPP was synthesized in a known one-pot reaction. Although its crystal structure is well known, ours is the first known solvate of CoTPP containing a saddle-shaped macrocycle conformation. There is a wide variety of known non-planar porphyrins that reveal that the symmetry type and the magnitude of macrocycle distortions can modulate several CoTPP biochemical reactions in vivo and also alter many of its physicochemical properties [5,6]. In light of this, the synthesis and the X-ray structure of this new solvate form of CoTPP are reported here along with a detailed examination of its conformational features and crystal assembly. We also discuss theoretical insights regarding the structural relationships between the macrocycle and the phenyl conformations by using a potential energy surface (PES) calculation of a key torsional angle around the bridge bond between these moieties. This allowed us to assign the symmetry loss we observed in our triclinic structure to the saddle-shaped macrocycle distortion as a result of an unlike phenyl twisting.

Experimental

Synthesis

Cobalt (II) *meso*-tetraphenylporphyrin (CoTPP) was prepared using an adaptation of the procedure reported by Mirafzal for the synthesis of manganese(III) *meso*-tetraarylporphyrins (Scheme 1) [7]. CoTPP was synthesized by reacting benzaldehyde (2.47 mL, 0.024 mol), pyrrole (1.70 mL, 0.024 mol), cobalt (II) acetate (3.005 g, 0.012 mol) and 2.707 g of 2,4,6-trichlorophenol. Pyrrole and benzaldehyde were previously distilled. This mixture was kept at reflux temperature for 5 h. The progress of the reaction was monitored by the appearance of the characteristic metalloporphyrin absorption bands at 410 and 527 nm (measured in dichloromethane solution). The UV–Vis spectra were recorded at different time intervals using a conventional quartz cell (light path 10 mm) on a Shimadzu UV-3600 spectrophotometer. Next, the reaction mixture was cooled at room temperature and washed with NaOH (0.1 mol L⁻¹). CoTPP was purified on a neutral alumina column eluted with a mixture of cyclohexane and dichloromethane (3:1, v/v). The reaction yield was approximately 22%.

CoTPP was characterized by FT-IR spectroscopy and single crystal X-ray diffraction. FT-IR measurements were performed on a Bomem MB-102 spectrophotometer on KBr pellets prepared using a hydraulic press (mixtures comprised 200 mg of KBr and 1 mg of sample). The spectrum was recorded as an average of 128 scans at a resolution of 4 cm⁻¹ from 4000 to 400 cm⁻¹.

Single crystal X-ray diffraction analysis

A total of 3 mg of CoTPP was dissolved in 4 mL of a dichloromethane/ethanol mixture (3:1 v/v). Needle-shaped crystals of CoTPP were obtained after 4 days by slow evaporation of the solvent at 5 °C.

Needle-shaped crystals of CoTPP were obtained from a 3:1(v/v)dichloromethane and ethanol mixture. Diffraction data were collected at a low temperature on an Enraf-Nonius Kappa-CCD diffractometer with graphite monochromatic Mo K α radiation $(\lambda = 0.71073 \text{ Å}), T = 150 \text{ K}).$ For low temperature experiments, a cold N₂ gas-blowing cryogenic device (Oxford Cryosystem) was used. The diffraction intensities were processed and scaled with the HKL Denzo-Scalepack software [8]. Because the crystal size was small (medial crystal size x = 0.09 mm) and the absorption coefficient was not very high ($\mu = 0.643 \text{ mm}^{-1}$), no absorption correction was applied [9]. The structure was solved using direct methods of structure factors phase retrievel [10]. A full-matrix least-squares refinement of F^2 with anisotropic thermal parameters for all of the non-hydrogen atoms was performed using SHEL-XL-97 [11]. H atoms were placed on carrier atoms on a stereochemical basis and refined with fixed geometry with an isotropic displacement parameter of 1.2 times the value of the equivalent isotropic displacement parameter of the carrier atom. A weighting scheme of the form $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3)$, was introduced in each case.

Disordered sites were found in the asymmetric unit around dichloromethane molecules. Trial refinements were used with the split-atom approach for these extra sites. A classical split-atom model with two dichloromethane positions resulted in the best structural refinement from a statistical and convergence point of



Scheme 1. One-pot synthesis of cobalt (II) meso-tetraphenylporphyrin (CoTPP).

Table 1

Crystal data and structure refinement parameters for the dichloromethane solvate of CoTPP.

Empirical formula (C ₄₄ H ₂₈	N_4Co ·(CH_2Cl_2) _{0.6}
Formula weight 722.25	
Temperature (K) 150(2)	
Crystal size (mm ³) 0.15×0	0.09 imes 0.05
Wavelength 0.71073	3
Crystal system Triclinia	2
Space group P ₁	
a (Å) 9.171(1	2)
b (Å) 13.24(3)
c (Å) 14.79(3)
α (°) 79.74(7)
β(°) 86.78(3)
γ (°) 72.70(5)
V (Å ³) 1687(5))
Z 2	
$D_{\rm c}({\rm Mg/m^3})$ 1.422	
Absorption coefficient (mm ⁻¹) 0.643	
F(000) 744.1	
θ range for data collection (°) 2.94–23	8.14
Reflections collected 8199	
Independent/observed refls. $[I > 2\sigma(I)]$ 4676/24	$464 (R_{int} = 0.1245)$
Completeness to θ_{max} (%) 97.8	
Data/restraints/parameters 4676/55	5/497
GOF on F^2 0.940	
Final <i>R</i> indices $[I > 2\sigma(I)]$ $R_1 = 0.0$	641, <i>wR</i> ₂ = 0.1205
<i>R</i> indices (all data) $R_1 = 0.1$	481, <i>wR</i> ₂ = 0.1481
Largest diff. peak and hole ($e Å^{-3}$) 0.389 a	nd –0.490

view. A SHELXL [11] (second FVAR instruction) restraint was applied to refine the ratio of the two disordered dichloromethane units with their site occupation factors (s. o. f.) adding to ca. 0.6, namely, 0.526(4) and 0.070(2). The details of the unit cell parameters, X-ray data collection, and structure refinement are shown in Table 1. The crystallographic software PARST95 [12], PLATON [13], WinGX [14], ORTEPIII [15] and DIAMOND [16] were also used in this study.

Potential Energy Surface (PES) calculation for phenyl conformation

The electronic structure of a single CoTPP molecule was theoretically investigated with Density Functional Theory (DFT) using the B3LYP hybrid exchange-correlation function. The Sapporo non-relativistic double zeta core/valence (SPK-DZC) [17] basis set implemented in the GAMESS program [18] was used in all calculations. Based on the molecular conformations from the X-ray structures of CoTPP (CSD Refcode TPORCP12 [19]) and its dichloromethane solvate elucidated here, the rigid potential energy curve was computed over a rectangular grid for the selected C6-C5-C21-C26 dihedral angle (see Fig. 1 for atom labels) to describe the conformation of the phenyl moiety (Ph1), which differs in the dichloromethane solvate from the three other known CoTPP structures. In these calculations, no geometry optimizations or symmetry constraints were used on the single molecule of CoT-PP. The selected dihedral angle was forced to rotate by 5° to obtain the energy profile for the phenyl conformation analysis of the isolated molecule. The PES curves were fitted using a cubic smoothing spline. To provide robust cooperation between the experimental and theoretical results of the full geometry, optimizations of both of the molecular species were computed with a gradient root mean square smaller than 2×10^{-4} using the same calculation described above but without symmetry constraints.

Results and discussion

Intramolecular structure from a single-crystal X-ray diffraction technique

A new dichloromethane solvate form of CoTPP was crystallized in a dichloromethane/ethanol mixture (3:1 v/v). This crystallization procedure differs from that used for the preparation of the non-solvated CoTPP phase, which crystallized directly from the reaction medium of the macrocycle synthesis, using dimethylformamide as a solvent [19]. Its structure was determined using singlecrystal X-ray diffraction. Fig. 1a shows its molecular structure and the atom labeling schemes employed. This solvate form crystallized in the triclinic space group *P*ī with unit cell parameters (see Table 1) distinct from the non-solvated CoTPP (a = b =15.062(4) Å, c = 13.954(5) Å, $\alpha = \beta = \gamma = 90^{\circ}$, V = 3178(2) Å³), which crystallizes in the tetragonal space group I-42*d*, similar to other metallotetraphenylporphyrins.

In the CoTPP tetragonal structure determined by Nascimento [19] (CSD Refcode TPORCP12), the N–Co–N bond angles and the Co–N bond distances have values of 178.60(12)° and 1.949(2) Å, respectively. In the solvate triclinic structure, the N1–Co1–N3 and N2–Co1–N4 bond angles are 171.28(18)° and 170.79(18)°, respectively, with Co–N bond distances in the range of



Fig. 1. (A) Ortep diagram of CoTPP solvate. Displacement ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level (hydrogen atoms are arbitrarily scaled). Ellipsoids of the non-hydrogen dichloromethane atom fractions in the disordered positions of minor occupancy are drawn as boundaries, and open lines indicate bonds between these atom fractions. (B) A diagram of the porphyrinate core showing the displacements of atoms in units of 0.01 Å³ from the mean plane at the 24-atom core.



Fig. 2. View along the porphyrin mean plane detaching the saddle-shaped conformation of CoTPP (pyrrole fragments indicated by arrows are alternately below and above the mean plane) in (A) the dichloromethane solvate form (this study) and the ruffled distortion (pyrrole fragments stay near the mean plane) adopted in (B) the non-solvated tetragonal form (CSD Refcode TPORCP12). Phenyl rings are labeled in panel (A) to highlight the differences in the Ph1 conformation from the other benzene moieties, therefore abolishing the -4-fold axis symmetry found in (B). Hydrogens were omitted for clarity in both panels.

1.925(6)–1.967(5) Å. These structural differences between the two crystalline forms may be a consequence of the conformation adopted by the porphyrin macrocycle. It is well known that planar porphyrins are an exception rather than a rule and that distortions can be imposed on the macrocycle by several factors: (1) packing constraints in the crystal, (2) steric crowding caused by peripheral substituents of the porphyrin ligand, (3) the effects of intramolecular interactions between atoms of the axial ligands and the porphyrinate core, (4) intermolecular interactions, typically between two porphyrins ligands, i.e., dimeric interactions, and (5) the coordination requirements of the central metal ion itself [20]. More specifically, these distortions can be classified into 5 different types: ruffling (B1u), saddling (B2u), doming (A2u), waving (Eg) or propelling (A1u). The most common deformations observed for porphyrins and metalloporphyrins are ruffling and saddling. In all of the tetragonal structures of CoTPP available in the Cambridge Structural Database [21] (CSD Refcodes: TPORCP, TPORCP02, TPORCP11, TPORCP12), the ruffled core deformation is the most prevalent. This type of distortion is characterized by a twisting of pyrrole rings around the Metal-N bonds, which leads the meso carbon atoms to be alternately displaced below and above the mean plane of the 24-atom core.

In the triclinic solvate form of CoTPP, the displacements of the core atoms from the mean 24-atom plane (Fig. 1b) suggest that the macrocycle mainly adopts a saddle conformation with pyrrole units alternating between being below (-) or above (+) the mean plane and the *meso* carbon atoms near (±) or in (0) the mean plane (Fig. 2). The maximum deviations from the porphyrin mean plane are $-0.716(5)^{\circ}$ for C7 and $0.700(5)^{\circ}$ for C3.

Although some spectroscopic studies have shown a relationship between macrocycle non-planarity and the positions of the electronic and vibration bands, no significant differences were found in the UV-Vis or FT-IR spectra of the powder CoTPP samples used in the crystallization experiments [6,22]. As is commonly described in the literature [23], an intense absorption band (the Soret or B band) and another less intense (Q band) were observed in CoTPP samples at 410 and 527 nm, respectively. The main IR bands were assigned to (cm⁻¹) 1599, 1443, 1348, 1070, 1004, 796, 750, 701, and 466. Consequently, the spectroscopic techniques used in this work (UV-Vis and FT-IR) did not provide any new information about the macrocycle distortion but were used to ensure the homogeneity of the CoTPP that was synthesized. Previous studies were carried out with the three crystallographic forms of nickel (II) octaethylporphyrin (NiOEP) (planar triclinic A and B forms and the ruffled tetragonal form) using Raman spectroscopy and demonstrated that Raman lines are sensitive to changes in the porphyrin conformation. There were differences in the frequency of the vibrational modes for the crystallized and solution-phase samples of NiOEP [22]. Unfortunately, crystals of the dichloromethane solvate of CoTPP rapidly desolvate when they are removed from the mother solution and lose structural order (no X-ray diffraction is observed). X-ray diffraction data collection was only achieved while quenching the crystal at 150 K. This solvent-loss phenomenon is thought to be a consequence of the CoTPP channel solvate nature because of very weak contacts between CoTPP and the solvent molecules in the channels (see below).

Recently, a study of CoTPP molecules adsorbed on a Ag (111) surface showed that the porphyrin macrocycle adopts a saddleshaped conformation and keeps this geometry even after being exposed to CO. The study also concluded that this type of distortion induces a *cis*-carbonyl geometry, with CO binding to two spatially distinguished sites on CoTPP [24]. Although these results are of particular interest for understanding the biochemical reactions, they were obtained using a scanning tunneling microscope and thus do not provide any insight into how CoTPP molecules are assembled in the crystal. To the best of our knowledge, the sad-dle-like conformation has been reported in crystals of coTPP. This study presents the first report of a crystal structure of CoTPP with a saddle-shaped conformation.

The triclinic and tetragonal structures of CoTPP differ in their phenyl orientations. For the tetragonal form (CSD Refcode TPORCP12), the dihedral angle between the mean planes of the 24-atom core and each phenyl ring is 80.23(14)°, which is consistent with data reported in the literature for several tetraphenylporphyrins where peripheral phenyl groups are essentially orthogonal for tetragonal forms.

In the triclinic form, the dihedral angles are different for each phenyl ring, causing a decrease in symmetry in the dichloromethane solvate form compared to the non-solvated tetragonal form. The conformation of one of the phenyl rings is remarkably different from the other three, which exhibit very similar dihedral angles. The phenyl rings bonded to C5 (Ph1), C10 (Ph2), C15 (Ph3) and C20 (Ph4) form dihedral angles of $51.63(14)^\circ$, $83.74(14)^\circ$, $82.31(14)^\circ$ and $82.38(15)^\circ$ with the porphyrin core mean plane, respectively.

A small dihedral angle of 58.23(5)° has also been reported for one of the phenyl rings in the saddle structure of the vanadyl tetrakis(pentafluorophenyl)-porphyrin dichloromethane solvate (CSD Refcode SAWQEM). In this case, the deviation was attributed to weak intermolecular interactions between the dichloromethane solvent molecule and the fluorine atoms of the phenyl ring. However, in the CoTPP solvate structure, the dichloromethane molecule is located near to Ph2 and Ph4, which is far from Ph1 (Fig. 3).

Theoretical approach to intramolecular structure

To approach the relationship between the macrocycle and the phenyl conformations, we calculated a PES scan for the C6–C5–C21–C26 dihedral angle (according to atom labels in Fig. 1) for a single CoTPP molecule in both the non-solvated (CSD Refcode TPORCP12 [19]) and dichloromethane solvate forms. Molecular conformations determined by single-crystal X-ray diffraction were used in the calculations without geometry optimization. The PES curves for this torsion angle on the bridge between the unique phenyl moiety in our structure and the macrocycle are depicted in



Fig. 3. (A) A view along the (100) plane reveals how CoTPP molecules propagate in [010] and [001]. *Cg1* and *Cg4* are the centroids calculated through the Ph3 (C33 to C38) and Ph2 (C27 to C32) carbon atoms (B) View of the CoTPP solvate along [100] (left) and [001] (right) illustrating the layered organization (A and B label inversion-symmetry related layers). Only dichloromethane fractions with the major s. o. f. are shown in both panels.

Fig. 4. To make the comparison easier, the curves were both shifted to have their minimum energy at zero. The potential energy curves of CoTPP in its non-solvated and solvate forms were shifted by 3294.23704 and 3293.603138 atomic units, respectively. The CoT-PP in the non-solvated tetragonal structure has the lowest energy. Its minimum energy for the selected torsional angle occurs, as found in its crystal, at 102.8° (or 282.8° due to the 2-fold rotational symmetry along the C5–C21 bond), while the dichloromethane solvate form has a minimum energy with a dihedral angle at 62.3° (or 242.3°, as depicted in Fig. 4 by the black arrow, due to



Fig. 4. Potential energy curve (rigid scan) around the C6–C5–C21–C26 torsion angle of CoTPP in both the non-solvated and solvate forms. The arrows indicate one of two minimum energy values in each structure due to the 2-fold rotational symmetry along the C5–C21 bond (these minimum values are at 62.3° and 242.3° in the solvate form and at 102.8° and 282.8° in the non-solvated form).

the 2-fold rotational symmetry also along the C5–C21 bond). This value is in agreement with the experimental value measured in the crystal structure of the solvate $[67.3(7)^{\circ}]$. This indicates that the saddle macrocycle conformation can explain the Ph1 twist we observed in our structure. Conversely, if the intermolecular interaction pattern was the primary driver of the Ph1 conformation in the solvate form, the minimum energy for this torsion angle could assume a very different value from what was observed in the single-crystal structure. Furthermore, the equivalent torsion angle at the minimum energy value for the saddle distortion (62.3°) has a higher energy in the ruffled conformation, as shown in Fig. 4. Without taking into account the energetic contributions of intermolecular contacts in the crystal, this allows us to state that the ruffled conformation observed in the non-solvated form hinders the formation of the Ph1 torsion we observed in the dichloromethane solvate. It is only attainable in the saddle macrocycle conformation. In summary, the formation of the torsion angle around the C5-C21 bond axis is primarily driven by intramolecular forces and not by intermolecular forces such as weak contacts with CH₂Cl₂ or moieties of neighboring CoTPP molecules. In addition, the high energy of CoTPP in the dichloromethane solvate form explains its instability in the absence of the mother solution, as mentioned above.

The torsional barrier is also bigger for the lowest energy CoTPP molecule in the non-solvated form than it is for the highest molecule in the solvate form. The potential curve of the dichloromethane solvate shows a less symmetrical shape in the minimum region compared to the lowest energy structure. This occurs because the Ph1 conformation is very different from those of Ph2, Ph3 and Ph4 in our structure, and the loss of molecular symmetry is reflected in its PES curve. In contrast, the lowest energy form is



Fig. 5. Comparison of the optimized (green) and experimental (cyan) structures of CoTPP in (A) the dichloromethane solvate and in (B) the non-solvated form. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

 Table 2

 Summary of the intermolecular interactions in the dichloromethane solvate of CoTPP.

Donor–H· · · Acceptor	D–H (Å)	D· · ·A (Å)	H···A (Å)	$D-H\cdots A(^{\circ})$
$\begin{array}{c} C25-H25\cdots Cg1^{a,(i)}\\ C28-H28\cdots Cg3^{(ii)}\\ C44-H44\cdots Cg2^{(iii)}\\ \end{array}$	0.93 0.93 0.93	3.754(7) 3.456(2) 3.355(2)	3.11 2.54 2.45	127.8 169.2 163.2
$C41-H41\cdots Cl2^{(IV)}$	0.93	3.742(6)	2.94	145.4

^a *Cg1*, *Cg2* and *Cg3* are the centroids calculated through the atoms C33–C34–C35–C36–C37–C38, N2–C6–C7–C8–C9 and N1–C1–C2–C3–C4, respectively. Symmetry codes: (i) x, y, z – 1; (ii) –x + 1, –y, –z + 1; (iii) –x + 2, –y, –z + 1; (iv) –x + 2, –y–1, –z + 2.

highly symmetrical with identical phenyl conformations. Consequently, all of the carbons and hydrogens of each phenyl ring always band on the same side.

The full DFT optimization of the molecular conformation of the free CoTPP molecule, using the crystalline structures of the non-solvated and solvate forms as starting geometries, has produced structures that are remarkably similar to those seen in the crystallographic asymmetric units. The DFT-optimized and experimental structures were compared by superimposing all of the non-hydrogen atoms and using a least-squares algorithm that minimizes the distances between the atoms (Fig. 5). The superimposed atoms of the experimental (single-crystal structure) and theoretical (DFT optimization) CoTPP had root mean square deviations of 0.1066 Å and 0.0387 Å in the dichloromethane solvate and non-solvated (CSD Refcode TPORCP12 [19]) forms, respectively.

Intermolecular structure from single-crystal X-ray diffraction technique

Analysis of the crystal packing revealed that Ph1 could form a weak $C-H\cdots\pi$ contact as a hydrogen donor, namely, $C25-H25\cdots Cg1^{(i)}$, where Cg1 is the centroid calculated through the Ph3 carbon atoms [symmetry code (i) = x, y, z - 1]. Although the $C25-H25\cdots Cg1^{(i)}$ angle is still below the optimal value of 180° for a strong $C-H\cdots\pi$ interaction (127.8° with a $C25\cdots Cg1$ distance of 3.754(7) Å), this type of contact may explain the small dihedral angle of $51.63(14)^\circ$. The resulting 1D network (Fig. 3a) can be envisaged as an infinite array of porphyrins along the [001] direction, linked together by $C-H\cdots\pi$ interactions.

This type of 1D network can be extended by forming weak contacts with CH₂Cl₂ (see below) to create a 2D motif where porphyrins stack on top of each other, forming layers parallel to the (110)lattice plane (Fig. 3b). The layers are related by inversion centers in such a way that the porphyrin of one layer overlaps parallel to the [100] on the porphyrin of another plane in an offset face-to-face fashion. The stacking distance between the porphyrin planes was calculated through the center of the 24-atom core (Fig. 1b) of 3.734(8) Å, and a stacking slippage of 3.826(4) Å was the distance between the N1-Co1-N3 planes. As a consequence, two interactions are observed between certain pyrrole groups and the metal atom: $Co \cdot \cdot Cg2^{(ii)}$ (3.388(2) Å) and $Co \cdot \cdot Cg3^{(iii)}$ (3.415(2) Å), where Cg2 and Cg3 are the centroids calculated through the atoms N2-C6-C7-C8-C9 and N1-C1-C2-C3-C4, respectively [symmetry codes: (ii)=-x + 1, -y, -z + 1, (iii)=-x + 2, -y, -z + 1]. Other weak intermolecular interactions also contribute to the structural stability of these layers, namely, contacts C28-H28...Cg3(ii) and C44-H44 $\cdot Cg2^{(iii)}$, with separations of 3.456(2) Å and 3.355(2) Å, respectively (Table 2).

The horizontal packing of these layers is not efficient, which results in the formation of wide holes between the layers. The holes propagate through the crystal parallel to the *a*-axis and are occupied by dichloromethane molecules from the surrounding crystallization environment (Fig. 6). It is important to note that only a fraction of the dichloromethane was found in the asymmetric unit, as deduced from the refinement. This split-atom model gives better *R*-factors with a low residual electron density in the unit cell and refinement convergence.

As mentioned above, the crystal is not stable outside the mother solution, and a loss of solvent drastically changes the crystal's macroscopic morphology as a result of structure disruptions. Several porphyrin clathrates with different architectures and guest molecules have been extensively described [1,3,4]. Goldberg and



Fig. 6. Two-dimensional arrays of CoTPP molecules illustrating (A) the channels filled with dichloromethane molecules and (B) the intermolecular interactions between CoTPP molecules and between CoTPP and solvent molecules. Only hydrogen atoms involved in intermolecular interactions are shown. *Cg2, Cg3* and *Cg4* are the centroids calculated through the atoms N2–C6–C7–C8–C9, N1–C1–C2–C3–C4 and C33–C34–C35–C36–C37–C38. Only dichloromethane fractions with the major s. o. f. are shown in both panels.

co-workers have demonstrated that the removal of guest molecules from ZnTPP clathrates results in the formation of an isostructural desolvate material whose X-ray powder pattern is identical to that of the non-solvated material [1b]. This emphasizes the role of dichloromethane molecules in driving macrocycle conformation and packing in the lower crystallographic symmetry crystal phase of CoTPP. The dichloromethane molecules are also involved in weak C-H---halogen interactions that bind to porphyrins in adjacent layers, such as the C41-H41...Cl2^(iv) contact [symmetry code (iv)=-x + 2, -y-1, -z + 2] (Table 2 and Fig. 3a). An additional host-guest halogen $\cdots \pi$ contact between the Cl1 of dichloromethane and the Ph2 of porphyrin was established, with a $Cl1 \cdots Cg4^{(ii)}$ separation of 3.817(2) Å, where Cg4 is the centroid calculated through the Ph2 carbon atoms (Figs. 3 and 6). These contacts involving both of the chlorine atoms of dichloromethane are responsible for the alternating CoTPP and solvent molecules in the [0–11] direction (Fig. 3).

Conclusion

In summary, a new solvate crystal form of CoTPP has been isolated and characterized by single-crystal X-ray diffraction. This form exhibits a distinct saddle-shaped macrocycle distortion as a result of the crystallization environment. Although this type of conformation has been recently reported in a study of CoTPP molecules adsorbed onto an Ag (111) surface, we have employed scanning tunneling microscopy to examine the conformational features. This is the first time that this conformation has been observed in a CoTPP crystal, and the resulting supramolecular assembly can be explained.

The saddle-shaped macrocycle conformation depends on a unique phenyl twist differing from the other three phenyls in CoTPP and is supported by PES calculations for the torsional angle around the bridge between the phenyl and pyrrole rings of CoTPP in both the non-solvated and solvate forms. Therefore, this macrocycle conformation, rather than intermolecular interactions, is responsible for the loss of both molecular and crystal symmetries. The intermolecular interactions appear to have a meaningless role in driving the unique phenyl torsion angle.

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Appendix A. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 864256. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or e-mail: http:// deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.molstruc.2014.08.001.

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