Solid-state Porphyrin Interactions with Oppositely Charged Peripheral Groups

W. Robert Scheidt[a,*], **Beisong Cheng**[a], **Allen G. Oliver**[a], and **John A. Goodwin**[a,b]

[a]Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA
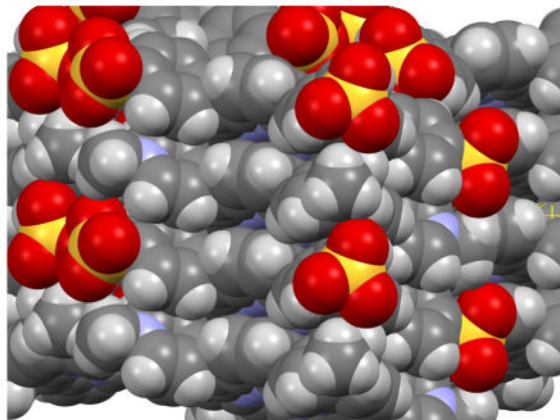
[b]Department of Chemistry and Physics, Coastal Carolina University, Conway, SC 29528, USA

Abstract

The crystallization and the crystal and molecular structure of a very slightly soluble electrostatically interacting pair of porphyrins is described. The tetra-anion 5,10,15,20-tetrakis-(4-sulfonatophenyl)-21,23H-porphyrin $[H_2TPPSO_3]^{4-}$ and the tetra-cation 5,10,15,20-tetra(N-methylpyridyl)21H,23H-porphyrin $[H_2TMePyP]^{4+}$ are found to form an alternating one-dimensional stack that is stabilised by electrostatic interactions between the porphyrin rings but also by $\pi-\pi$ interactions between all substituted phenyl rings in the ensemble. The resulting interactions between the porphyrins is exceptionally tight.

Graphical Abstract

The solid-state interaction of oppositely charged porphyrins leads to a tightly stacked 1-D chain with both electrostatic and $\pi-\pi$ interactions.

*Correspondence to: W. Robert Scheidt, Scheidt.1@nd.edu, fax: +1 574-631-5938.

Introduction

The initial reports on the properties of species formed by pairing cationic and anionic porphyrin derivatives were by Shimidzu and Iyoda [1], Gaspard [2], and by Linschitz and coworkers [3, 4]. This work was initially motivated by noting that closely coupled porphyrinic structures are involved in bacterial [5] and green plant photosynthesis [6]. Since that time, there have been a number of additional reports that involve the idea of electrostatically paired rings all without the participation of covalent interactions [7].

A number of solution studies of electrostatically interacting rings (porphyrins and/or phthalocyanines) have shown 1:1 [8, 9, 10, 11] or 2:1 [12, 13] stoichiometry and where the rings are either free bases or metallo derivatives. Electrostatically interacting pairs have also been used to form multi-electron electrocatalysts [14, 15].

To date, a solid-state structure of such electrostatically interacting species has not been reported. [16] Herein we report the X-ray crystallography study on an electrostatic "pair" and methods useful for obtaining crystalline material of this type. The interaction of two oppositely charged porphyrin species, the tetra-anion 5,10,15,20-tetrakis-(4-sulfonatophenyl)-21,23H-porphyrin $[H_2TPPSO_3]^{4-}$ and the tetra-cation 5,10,15,20-tetra(N-methylpyridyl)21H,23H-porphyrin $[H_2TMePyP]^{4+}$ (Figure 1) should lead to interesting solid-state structures owing to their electrostatic interactions. Especially note that the dimensions of the two species are commensurate. In addition to the possible formation of face-to-face heterodimers, other possibilities are 1-D linear or 2-D solid-state networks. Recently, the interaction of $[Zn(TPPSO_3(H_2O)]^{4-}$ and $[Sn(TMePyP)(H_2O)_2]^{4+}$ has been shown to form a 2-D network. [18]

Experimental Section

The free base porphyrin salts, $Na_4[H_2TPPSO_3]$ and $[H_2TMePyP]Cl_4$, were purchased from Midcentury Chemical and used without further purification. Mixing equivalent amounts of methanol solutions of $Na_4[H_2TPPSO_3]$ and $[H_2TMPyP]Cl_4$ at room temperature gave an "immediate precipitate." The mixture was stirred for one hour, the dull red solid product was harvested by centrifugation and washed six times with methanol. A completely colorless supernatant was never achieved suggesting that substantial amounts of coprecipitated starting materials are present within the solid matrix of the amorphous $[H_2TMePyP–H_2TPPSO_3]$.

Obtaining single crystals of the electrostatically interacting $[H_2TMePyP]^{4+}–[H_2TPPSO_3]^{4-}$ system is complicated by its extremely low solubility. A number of different crystallization experiments failed to provide crystals adequate for a single crystal X-ray study. Attempts to use gels [19] to overcome this complication have thus far been unsuccessful. In addition, the gel crystallization process has pH-sensitivity requirements that rule out the use of gels for certain water-soluble metalloporphyrin derivatives. Eventually crystals of the electrostatically interacting complex $[H_2TMePyP–H_2TPPSO_3]·5H_2O$ were obtained by allowing 3×10^{-3} M aqueous solutions of $Na_4[H_2TPPSO_3]$ and $[H_2TMePyP]Cl_4$ to slowly diffuse together in a U-tube assembly shown in Figure 2. The middle section of the tube was

filled with propylene glycol which was then frozen. Each porphyrin solution (~2.5 mL) was carefully added to one leg of the U-tube as shown. The two porphyrin solutions were then allowed to diffuse together in the middle section. After standing approximately 1 1/2 yrs, the crystals that had formed were removed by breaking open the tube. Crystal specimens were stored in a refrigerator until use.

A deep blue crystal with approximate dimensions of $0.33 \times 0.45 \times 0.06$ mm was mounted on a glass fiber and coated with epoxy cement. Crystals were examined on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Cu Ka radiation ($\bar{\lambda} = 1.54184$ Å) and found to be monoclinic (space group $P2_1/c$) containing four porphyrin rings, two of each type [20]. For an *ordered* structure the asymmetric unit of structure must contain two *half* porphyrin rings, each with required inversion symmetry, along with any required molecules of solvation (that might required for crystal stability). All subsequent details of structure solution and refinement are consistent with an ordered structure.

Results and Discussion

The X-ray crystal structure determination not only gives information about the molecular structures of the two porphyrin free bases (negatively charged $[H_2TPPSO_3]^{4-}$ and the positively charged $[H_2TMePyP]^{4+}$) but also the solid-state interactions between them. We first describe the molecular structure of the individual porphyrin units and then the crystal structure of the entire electrostatically interacting ensemble.

Figure 3 shows the average values of the bond distances and bond angles in each of the two porphyrin cores. As is readily seen, the two porphyrin systems have quite similar metrical values. The most significant features are the values of the C_a–N–C_a bond angles that are consistent with the two inner hydrogen atoms of each porphyrin ring delocalized over all central nitrogen atoms [21]. The values of bond distances and angles otherwise do not need further comment. The radius of the central hole is 2.060 Å for $[H_2TMePyP]^{4+}$ and 2.056 Å for $[H_2TPPSO_3]^{4-}$. Also shown in Figure 3 are the deviations of the individual atoms from the mean plane of the 24-atom porphinato core. Deviations from exact planarity are seen to be small but do appear to show intra-stack correlations in the displacements (vide infra). In the $[H_2TMePyP]^{4+}$ cation, the dihedral angles of the peripheral 4-methylpyridyl rings with the mean plane of the core are 53.3° and 54.0°; peripheral phenylsulfonate rings form dihedral angles of 53.8° and 52.3° relative to its porphyrin core. These values are significantly smaller than the usually observed values (> 60°)[22] and reflect aspects of the tight interactions between the oppositely charged porphyrin cores as described below. Figures S1 and S2 display ORTEP diagrams of the two porphyrin ions with the crystallographically unique atoms labeled.

The interaction of the two oppositely charged porphyrin species self-assemble to form one-dimensional columns. Each ring is centered on an inversion center along the *a* axis with alternating anionic and cationic porphyrin molecules in the stack as shown in Figure 4. The centers of the two types of porphyrins are separated by 4.253 Å (*a/2*). The adjacent porphyrin rings are coplanar within 0.2°, with an interplanar spacing of 3.81 Å, although no

special requirements are imposed by the crystallographic symmetry. A space filling model of the electrostatically interacting columns is given in Figure S3.

Figure 5 illustrates the small lateral shift between a cofacial pair of porphyrin rings. The lateral (parallel) shift of ring centers is only 1.88 Å from a precise eclipsing of adjacent cores, but with a relatively large interplanar spacing of 3.81 Å. Figure 5 also shows another interesting feature of the crystal structure: the correlated positions of the peripheral, charged rings on the anion and cation. Adjacent N-methylpyridyl and phenylsulfonate rings are virtually parallel with dihedral angles between pairs of rings of 0.5 or 2.8° and, of course, extend over the entire stack length. These sulfonatophenyl–N-methylpyridyl ring alignments represent the closest possible approach of the oppositely charged peripheral groups (vide infra). These peripheral group contacts also lead to the alignment of the porphyrin core coordinate systems that are seen in Figure 5. The edge-on view of the [H_2TMePyP–H_2TPPSO$_3$] ensemble in Figure S4 further illustrates the intermolecular interactions between the oppositely charged porphyrins. Consistent with the crystallographic (translational) symmetry, the same interplanar spacing (~3.81 Å), center ⋯ center distance (4.253 Å), lateral shift (1.88 Å), and slip angle (26.4°) are applicable to any adjacent pair of porphyrins in the stack illustrated in Figures 4 and S4. These inter-ring interactions are the tightest known for pairwise interacting tetraarylporphyrin systems, where the inter-ring separations are comparable, but the center ⋯ center distances and hence the lateral shifts and slip angles are larger. These interactions are tighter than those seen for the dimeric interactions of π-cation derivatives of tetraarylporphyrins. [23, 24] See also Table XXIV of Reference 22 for further examples. The tightness of the current structure is also shown by the experimental density of 1.42 g/cm^3 compared to the the observed value of 1.22 g/cm^3 for the triclinic [25] and tetragonal [26] forms of H_2TPP.

The mutual parallel orientation of all five rings between any adjacent pair of porphyrins isparticularly evident. Figures 4 and 5 illustrates the interaction of the individual peripheral groups. Particularly note that any individual substituted phenyl ring interacts with two adjacent rings (of opposite charge) on both faces of the ring. Distances between phenyl ring centers range between 4.23 and 4.28 Å. The slipped rings, however, each have (two) interactions with perpendicular separations of 3.26 to 3.45 Å, with most 3.35 Å. These distances are those expected for attractive phenyl–phenyl π-π bonding. We can thus conclude that the solid-state structure of the stacked, alternating porphyrin rings is stabilized by both electrostatic interaction of the two oppositely charged porphyrin rings and π-π interactions between the substituted peripheral phenyl groups.

The 1-D stacked rings lead to a crystal structure with solvent channels containing hydrogen bonded water molecules as illustrate in Figure 6. There are five crystallographically unique water molecules or ten water molecules for each electrostatic porphyrin pair. There are a total of six unique hydrogen bonds; four are between the water molecules themselves and the final two are to oxygen atoms of the sulfonate groups. Each sulfonate group of the tetrasulfonated porphyrin has a single hydrogen bond. The O⋯O distances range between 2.720 to 2.921 Å.

In conclusion, the interactions of the oppositely charged porphyrin rings, negative $[H_2TPPSO_3]^{4-}$ and positive $[H_2TMePyP]^{4+}$, lead to a tightly stacked one dimensional chain. Stabilizing interactions between the rings in the stack not only include the electrostatic interactions of the oppositely charged porphyrin rings, but also strong $\pi-\pi$ interactions between the substituted peripheral phenyl rings.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

References and Notes

1. Shimidzu T, Iyoda T. Chem Lett. 1981:853–856.

2. Gaspard S. CR Acad Sci Paris. 1984; 298:379–382.

3. Ojadi E, Sulzer R, Linschitz H. J Am Chem Soc. 1985; 107:7783–7784.

4. van Willigen H, Das U, Ojadi E, Linschitz H. J Am Chem Soc. 1985; 107:7784–7785.

5. Deisenhofer J, Epp O, Miki K, Huber R, Michel H. J Mol Biol. 1984; 180:385–398. [PubMed: 6392571]

6. Katz JJ, Shipman LL, Norris JR. Ciba Found. 1979; 61:1–4.

7. (a) Maiya JR. J Porphyrins Phthalocyanines. 2004; 8:1118–1128.(b) Kano K. J Porphyrins Phthalocyanines. 2012; 16:148–155.(c) Hambright, P. Chemistry of Water Soluble Porphyrins. In: Kadish, KM.; Smith, KM.; Guilard, R., editors. The Porphyrin Handbook. Vol. Chapter 18. Academic Press; San Diego, CA: 2000. p. 129-200.

8. Geiger DK, Kelly CA. Inorg Chim Acta. 1998; 154:137–140.

9. Goodwin JA, Scheidt WR. J Phys Chem. 1990; 94:4432–4439.

10. Endisch C, Fuhrhop J-H, Buschmann J, Luger P, Siggel U. J Am Chem Soc. 1985; 118:6671–6680.

11. Eugster N, Sreenivasan KP, Su B, Girault HH. Langmuir. 2006; 22:1112–1120. [PubMed: 16430273]

12. Tasso TT, Moreira WC. J Porphyrins Phthalocyanines. 2012; 16:244–248.

13. Ruhlmann L, Nakamura A, Vos JG, Fuhrhop J-H. Inorg Chem. 1998; 37:6052–6059. [PubMed: 11670742]

14. D'Souza F, Hsieh Y-Y, Deviprasad GR. Chem Commun. 1998:1027–1028.

15. Chen J, Lever ABP. J Porphyrins Phthalocyanines. 2007; 11:151–159.

16. After this manuscript had been submitted, we learned of an earlier related study, [17] with the interaction of the H_2TPPSO_3 tetraanion with two different 5,10,15,20- tetra-N-alkylpyridyl porphyrins cations and the crystal structures of the products. Unfortunately, complete details of the structures are limited. The two species appear to form 1-D stacked structures of alternating positive and negatively charged porphyrins with the ions somewhat more loosely associated with each other than in that found for the structure reported herein.

17. Yamada Y, Matsumoto S, Yamada K, Nishino T, Mihara N, Sugimoto K, Tanak K. Chem Lett. 2014; 43:1377–1379.

18. Tian Y, Beavers CM, Busani T, Martin KE, Jacobsen JL, Mercado BQ, Swartzentruber BS, van Swol F, Medforth CJ, Shelnutt JA. Nanoscale. 2012; 4:1695–1700. [PubMed: 22310932]

19. Henisch, HK. Crystal Growth in Gels. Pennsylvania State University; University Park: 1970. Henisch, HK. Crystals in Gels and Liesegang Rings. Cambridge University; N. Y: 1988.

20. Crystal data for $[H_2TMePyP–H_2TPPSO_3]\cdot5H_2O$: monoclinic, space group $P2_1/c$, Z=2, a=8.506(2) Å, b=16.426(3) Å, c=29.288(3) Å, β=91.98(1)°, V=4089.7(13) Å^3, d_{calcd}=1.432Mg/m^3, R1(all

data)=0.1368, wR2=(all data,F)σ^2)=0.3331, GOF=1.913. CCDC-1422488 contains the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk

21. Scheidt, WR. Stereochemical Systematics for Porphyrins and Metalloporphyrins. In: Kadish, KM.; Smith, K.; Guilard, R., editors. Handbook of Porphyrin Science. Vol. 24. World Scientific; Singapore and Hackensack, NJ: 2012. p. 1-180.Coordination Chemistry and Materials

22. Scheidt WR, Lee YJ. Recent Advances in the Stereochemistry of Metallotetrapyrroles. Struct Bonding (Berlin). 1987; 64:1–70.

23. a) Scholz WF, Reed CA, Lee YJ, Scheidt WR, Lang G. J Am Chem Soc. 1982; 104:6791–6793.b) Erler BS, Scholz WF, Lee YJ, Scheidt WR, Reed CA. J Am Chem Soc. 1987; 109:2644–2652.

24. Gans P, Buisson G, Duee E, Marchon J-C, Erler BS, Scholz WF, Reed CA. J Am Chem Soc. 1986; 108:1223–1229.

25. Silvers S, Tulinsky A. J Am Chem Soc. 1967; 89:3331–3337. [PubMed: 6042769]

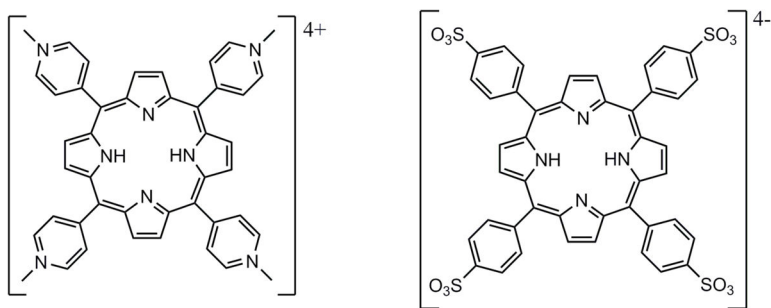26. Hamor MJ, Hamor TA, Hoard JL. J Am Chem Soc. 1964; 86:1938–1942.

Figure 1.
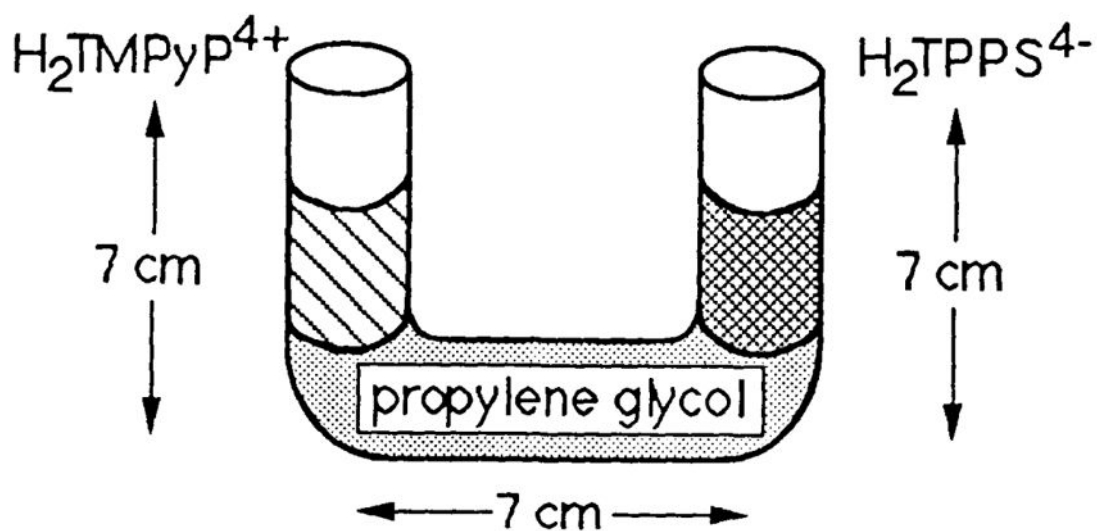Illustrations of [H$_2$TMePyP]$^{4+}$ and [H$_2$TPPSO$_3$]$^{4-}$.

Figure 2.
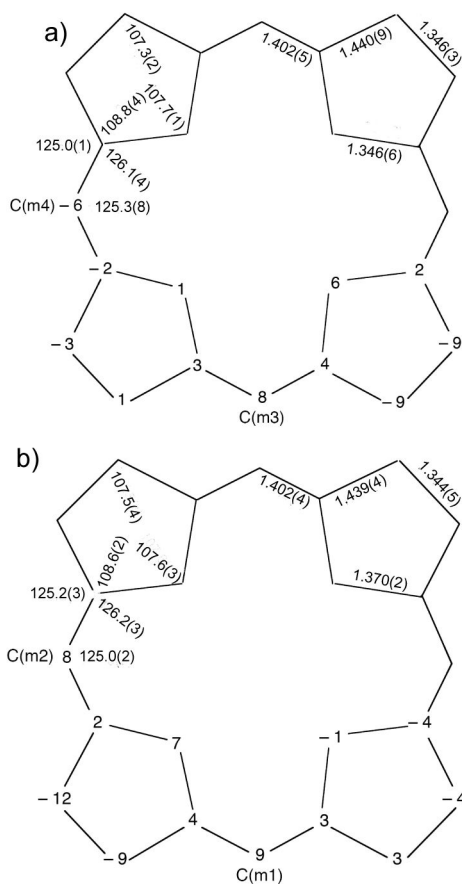Schematic illustration of the U-tube assembly used to prepare crystals of [H$_2$TMePyP–H$_2$TPPSO$_3$]·5H$_2$O. The diameter of the tube is 1 cm.

Figure 3.
Formal diagram of the porphyrin cores in (a) the $[H_2TMePyP]^{4+}$ cation and (b) the $[H_2TPPSO_3]^{4-}$ anion showing the averaged values of the unique classes of bond distances and angles in the 24-atom porphyrin cores. Values of the perpendicular displacement, in units of 0.01 Å, of each atom from the mean plane of the 24-atomn core is given.
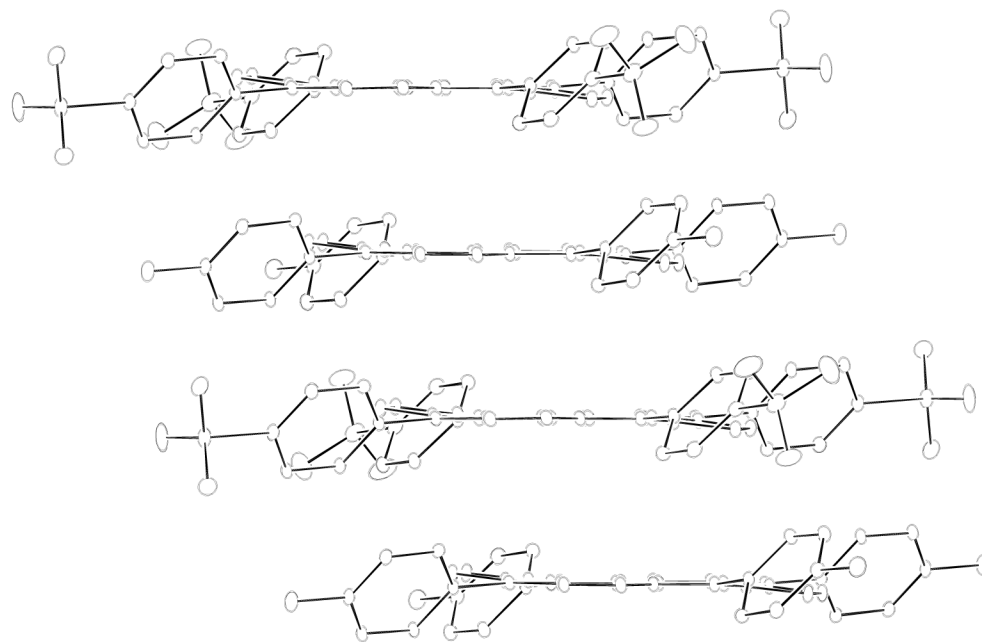
Figure 4.
ORTEP drawing (parallel projection) of four porphyrin rings in the stack of the electrostatically interacting [H_2TMePyP–H_2TPPSO$_3$]·5H_2O system. The center···center distance of 4.253 Å, the lateral shift of 1.88 Å, the slip angle of 26.4°, and the mean plane separation of 3.81 Å are applicable to any adjacent pair of porphyrin rings. Thermal ellipsoids are drawn at the 5% level.
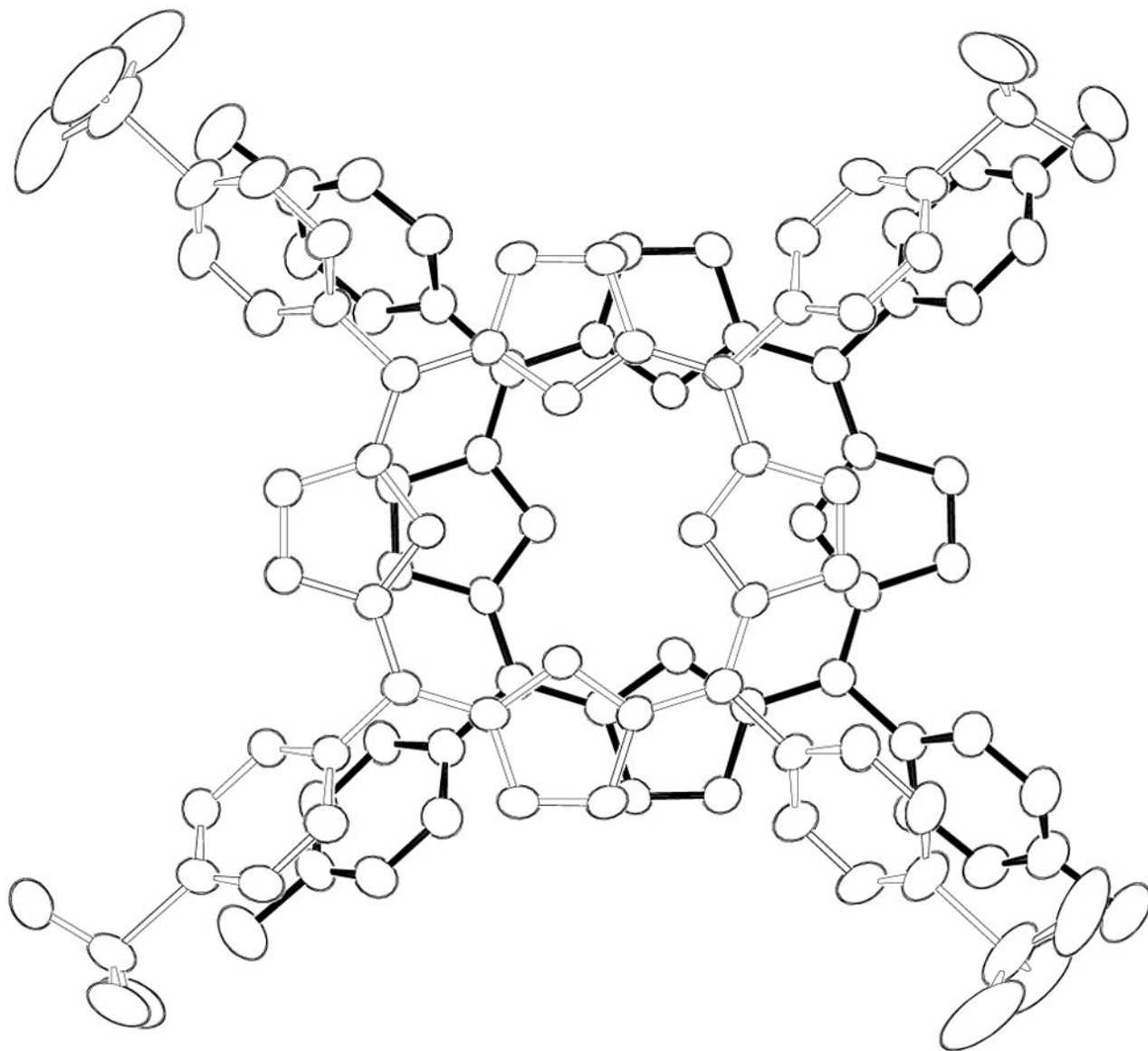
Figure 5.
ORTEP drawing of [H$_2$TMePyP–H$_2$TPPSO$_3$]·5H$_2$O illustrating the cofacial interaction between the peripherally charged cationic (heavy bonds) and anionic (lighter) rings. (parallel projection, 40% probability surfaces).
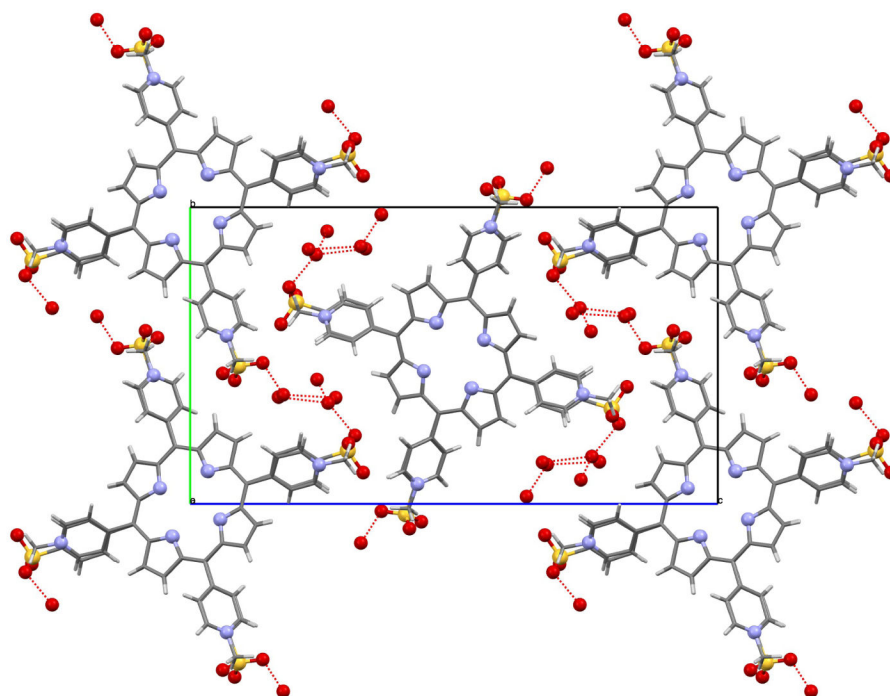
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ORTEP drawing of [H$_2$TMePyP–H$_2$TPPSO$_3$]·5H$_2$O illustrating the cofacial interaction between the peripherally charged cationic (heavy bonds) and anionic (lighter) rings. (parallel projection, 40% probability surfaces).