

Structure and Apparent Reactivity of the π -Cation Radical Derivatives of Zinc and Copper 5,10,15,20-Tetra(2,6-dichlorophenyl)porphyrinate

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The report that the π -cation radical complexes of 5,10,15,20-tetra(2,6-dichlorophenyl)porphyrinates have a near degenerate $^2A_{1u}/^2A_{2u}$ ground state has led us to examine their molecular structures. We wished to explore whether this near degeneracy leads to unusual structural features, namely, an alternating bond distance pattern in the 16-membered ring. The X-ray structure of the zinc complex of 5,10,15,20-tetra(2,6-dichlorophenyl)porphyrinate has a possible alternating bond distance pattern that could result from a pseudo-Jahn–Teller effect of coupled A_{1u} and the A_{2u} electronic states. In our attempts to prepare and crystallize additional π -cation radicals, we found an unusual reactivity at the molecular periphery of these porphyrin derivatives. The copper complex of 5,10,15,20-tetra(2,6-dichlorophenyl)porphyrinate reacts with thianthrenium perchlorate to give a β -thianthrenium derivative. The zinc complex reacts with iodine/silver perchlorate yielding neutral β -iodinated derivatives. We report the structure of the thianthrenium derivative $[\text{Cu}(\text{TCI}_2\text{PPTTh})\text{ClO}_4]$ and a symmetrically substituted β -tetraiodo derivative $[\text{Zn}(\text{TCI}_2\text{PPI}_4)]$. Crystal data: $[\text{Zn}(\text{TCI}_2\text{PP}^*)\text{OCIO}_3] \cdot \text{CH}_2\text{Cl}_2 \cdot 2\text{C}_6\text{H}_{14}$, monoclinic, space group Cc , $a = 12.516(2)$ Å, $b = 21.327(3)$ Å, $c = 22.764(3)$ Å, $\beta = 98.281(13)^\circ$, $V = 6012.8(16)$ Å³, $Z = 4$; $[\text{Cu}(\text{TCI}_2\text{PPTTh})]\text{ClO}_4 \cdot \text{CHCl}_3 \cdot \text{C}_6\text{H}_5\text{CH}_3$, orthorhombic, space group $Pca2_1$, $a = 14.7625(18)$ Å, $b = 12.220(2)$ Å, $c = 33.672(5)$ Å, $V = 6074.6(16)$ Å³, $Z = 4$; $[\text{Zn}(\text{TCI}_2\text{PPI}_4)(\text{THF})_2] \cdot 2\text{THF}$, triclinic, space group $P\bar{1}$, $a = 9.941(2)$ Å, $b = 11.615(2)$ Å, $c = 14.340(3)$ Å, $\alpha = 99.11(3)^\circ$, $\beta = 103.27(3)^\circ$, $\gamma = 106.61(3)^\circ$, $V = 1499.1(5)$ Å³, $Z = 1$.

Introduction

Metalloporphyrin π -cation radicals are important in the redox chemistry of a variety of biological systems.¹ The synthesis and solid-state structures of several π -cation radical derivatives have been described. One important class is the tetraarylporphyrins.^{2–4} Most of these species are simple aryls with no substituent on the phenyls. This set of porphyrin π -cation radicals has two characteristic solid-state conformational aspects. All such species with an open face form dimers with saddle-shaped porphyrato cores in which the pyrrole rings are alternately displaced above and below the mean plane of the core. Additionally, the phenyl groups tend to be coplanar with the porphyrato core. This particular conformation is attributed by Scheidt and Lee⁵ to steric conditions, since the more coplanar phenyl rings allows better overlap between the two 24-atom cores of one dimer. Dimer-

ization can be prevented by the presence of bulky groups on the ortho positions of the phenyl rings, which prohibits the near coplanarity of the peripheral aryls with the core. This case is illustrated by the structure of the π -cation radical $[\text{Cu}(\text{TMP}^*)]\text{[SbCl}_6]$.^{6,7} Its porphyrato core is almost planar, and the four phenyl rings are almost perpendicular to this plane; dimerization is thereby inhibited.

The structures of a number of octaethylporphyrin π -cation radicals are also known.^{8–10} These porphyrin molecules, with nonbulky β -pyrrole ethyl substituents, form very strongly coupled dimers with relatively small interplanar spacings when the π -cation radical derivative has an open face. A most surprising feature is the pattern of the bond distance values in the 16-membered ring of the porphyrato cores of several of these species. Usually the eight $C_a\text{--}N$ and eight $C_a\text{--}C_m$ bond distances are equivalent, consistent with a completely delocalized system. But, for $[\text{Zn}(\text{OEP}^*)(\text{OH}_2)]\text{ClO}_4$,⁸ $[\text{Fe}^{\text{III}}(\text{OEP}^*)(\text{Cl})]\text{ClO}_4$,⁹ and $[\text{Mg}(\text{OEP}^*)(\text{HOEt})]\text{[Mg}(\text{OEP}^*)(\text{OCIO}_3)]\text{ClO}_4$,¹⁰ two

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(7) Abbreviations: Porph, a generalized porphyrin dianion; TCI_2PP , the dianion of *meso*-(tetra-2,6-dichlorophenyl)porphyrin; TPP, the dianion of *meso*-tetraphenylporphyrin; OEP, the dianion of octaethylporphyrin; TMP, the dianion of *meso*-tetramesitylporphyrin; $\text{H}_2\text{TCI}_2\text{PPTTh}$, 2-(5'-thianthrenium)-5,10,15,20-tetra(2,6-dichlorophenyl)porphyrin cation; TCI_2PPI_4 , the dianion of 2,7,12,17-tetraiodo-5,10,15,20-tetra(2,6-dichlorophenyl)porphyrin; a raised dot in the formula of the porphyrin indicates a π -cation radical, e.g., TPP^* for the TPP π -cation radical.

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distinct sets of C_a-N and C_a-C_m bond distances were seen that describe a complete alternating pattern for the 16-membered ring.

Spiro et al. have suggested an explanation for this alternating bond distance pattern. The classic work of Gouterman¹¹ showed that the highest occupied porphyrin molecular orbital (HOMO), in D_{4h} symmetry, is that of either a_{1u} or a_{2u} symmetry, which are nearly degenerate. In the π -cation radicals, after removal of the electron, the remaining unpaired electron can reside in one of these two orbitals to yield either a ${}^2A_{1u}$ or a ${}^2A_{2u}$ state. Since only a small energy gap separates the A_{1u} and A_{2u} states, Spiro et al.¹² suggest that the ground and excited states are subject to vibronic coupling and that a pseudo-Jahn-Teller mixing of a_{1u} and a_{2u} will be seen. The resultant A_{2g} modes have the symmetry of a molecular rotation with possible alternation of bond lengths in the inner 16-membered ring. It is important to note that the alternating bond pattern is not always observed and indeed is clearly seen only in the OEP dimer derivatives described above. Bocian et al.¹³ have studied the electronic structure of the metallotetra(2,6-dichlorophenyl)porphyrin π -cation radicals with resonance Raman and EPR spectroscopy. They focused on the Zn(II) and Mg(II) complexes. It was expected that the metallo derivatives would have MO energies intermediate between those of tetraphenylporphyrin (a_{2u} HOMO) and tetra(pentafluorophenyl)porphyrin (a_{1u} HOMO). This reversal of the HOMO is due to the strong electron-withdrawing capacity of the perfluoro derivative.¹⁴ They concluded that the ground states of the $[M(TCl_2PP^*)]^+$ derivatives are indeed a admixtures of ${}^2A_{1u}/{}^2A_{2u}$. The four substituted phenyl groups are expected to be close to orthogonal to the porphyrinato core so that solid-state dimerization is unlikely.

Accordingly, we attempted to study the molecular structure of the π -cation radicals of tetra(2,6-dichlorophenyl)porphyrin. We expected to see an alternating bond distance pattern if this pattern can be attributed to a ${}^2A_{1u}/{}^2A_{2u}$ ground state mixing and if structures of adequate quality could be obtained. We initially chose the zinc(II) and copper(II) derivatives because of their relative solubility in organic solvents and relative ease of handling. We obtained crystals of the zinc π -cation radical complex; the structure showed a portion of an alternating bond distance pattern, and we report that structure herein.

In the course of attempting to prepare further crystalline derivatives with differing oxidants, we noted that the π -cation radical derivatives had significant reactivity at the molecular periphery. This reactivity appears to be that of nucleophilic attack on the π -cation radical. Thus the oxidation of $[Cu(TCl_2PP)]$ with thianthrenium perchlorate also leads to a β -thianthrenium derivative. An attempted oxidation of $[Zn(TCl_2PP)]$ with $AgClO_4/I_2$ leads to a mixture of β -iodinated derivatives. We report the structures of two such reaction products herein. We note that such reactivity with other tetraaryl π -cation radicals has not been reported.

Experimental Section

General Information. All manipulations were carried out under argon using a double manifold vacuum line, Schlenkware, and cannula techniques. Dichloromethane and chloroform were distilled from CaH_2 under argon. Hexanes and tetrahydrofuran were distilled from sodium/

benzophenone under argon. The free base 5,10,15,20-tetra(2,6-dichlorophenyl)porphyrin was synthesized as previously described.¹⁵ Zinc and copper were inserted into the free base via the DMF method.¹⁶ Thianthrenium perchlorate was prepared by literature procedures.¹⁷ **CAUTION!** These perchlorate-containing materials can detonate spontaneously and should be handled only in small quantities; other safety precautions are also warranted.¹⁸ UV-vis spectra were recorded on a Perkin-Elmer Lambda 6 spectrometer.

Preparation of $[Zn(TCl_2PP^*)OClO_3] \cdot CH_2Cl_2 \cdot 2C_6H_{14}$. $Zn(TCl_2PP)$ (60 mg, 0.063 mmol) and thianthrenium perchlorate (21 mg, 0.068 mmol) were placed in a 100-mL Schlenk flask. Dichloromethane (~20 mL) was added through a cannula, and the solution was stirred until the UV-visible spectra (λ_{max} 394 (shoulder), 419 (Soret), 550, 697 nm) was similar to the one described by Gross et al.¹⁴ (~18 h). The solution volume was reduced to half by evaporation under reduced pressure, transferred via cannula to a 50-mL Schlenk flask, and layered with hexanes for crystallization by liquid-liquid diffusion. After 4 days, dark purple single crystals had formed and were analyzed by X-ray diffraction. IR (KBr): ν (TCl_2PP^*) 1262–1263 cm^{-1} (strong).

Preparation of $[Cu(TCl_2PTh)]ClO_4 \cdot CHCl_3 \cdot C_6H_5CH_3$. $Cu(TCl_2PP)$ (47 mg, 0.049 mmol) and thianthrenium perchlorate (17 mg, 0.055 mmol) were placed in a 100-mL Schlenk flask. Dichloromethane (~20 mL) and ~20 mL of chloroform were added through a cannula, and the resulting solution was stirred for 5 h and became violet-green. Different mixtures of nonsolvents were used in attempts to grow single crystals usable for X-ray work. The crystal used for this study is the result of a slow diffusion of toluene and hexanes in the $CH_2Cl_2/CHCl_3$ solution.

Preparation of $[Zn(TCl_2PPL_4)] \cdot 4THF$. $Zn(TCl_2PP)$ (50 mg, 0.052 mmol), anhydrous silver perchlorate (21.6 mg, 0.104 mmol), and iodine (26 mg, 0.104 mmol) were placed in a 100-mL Schlenk flask. Tetrahydrofuran (~20 mL) was added through a cannula, and the solution was stirred. The solution rapidly became green, and a yellow-white precipitate appeared. After filtration under argon, the volume was reduced by one-half under reduced pressure. The solution was transferred via cannula to a 50-mL Schlenk flask and layered with hexanes for crystallization by liquid-liquid diffusion. Single crystals were obtained after several days. Subsequent reactions that were used to explore the products employed 8 equiv of I_2 and $AgClO_4$.

X-ray Diffraction Studies. All X-ray examination and data collection were performed at low temperature (130 ± 2 K) under the cold N_2 stream on an Enraf-Nonius FAST area detector with a graphite-monochromated Mo $K\alpha$ rotating anode source ($\lambda = 0.71073$ Å). All crystals were taken from the mother liquor, mounted on glass fibers, and placed as soon as possible under the cold stream on the diffractometer. A brief summary of crystal data and data collection parameters for the three structures is listed in Table 1; complete crystallographic details are included in the Supporting Information. Each structure was solved by using SHELXTL-86¹⁹ and refined with SHELXL-97.²⁰

$[Zn(TCl_2PP^*)OClO_3] \cdot CH_2Cl_2 \cdot 2C_6H_{14}$. A violet crystal of dimensions $0.43 \times 0.30 \times 0.17$ mm was studied. After several cycles of difference Fourier calculations, it was found that the porphyrin cation crystallizes with one dichloromethane molecule and two *n*-hexane molecules. The perchlorate anion is disordered over two positions with occupation factors of 0.62 and 0.38. The two positions have in common the chlorine atom and the oxygen O(1) atom coordinated to the zinc atom.

$[Cu(TCl_2PTh)]ClO_4 \cdot CHCl_3 \cdot C_6H_5CH_3$. A very thin triangular-shaped needle of dimensions $0.33 \times 0.03 \times 0.01$ mm was studied.

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Table 1. Crystallographic Details

	[Zn(TCl ₂ PP*)- (OCIO ₃)]	[Cu(TCl ₂ PPTTh)]- ClO ₄	[Zn(TCl ₂ PPI ₄)]
formula	C ₅₇ H ₅₆ Cl ₁₁ - N ₄ O ₄ Zn	C ₆₄ H ₃₆ Cl ₁₂ - CuN ₄ O ₄ S ₂	C ₆₀ H ₄₈ Cl ₈ L ₄ - N ₄ O ₄ Zn
fw	1316.38	1478.03	1745.59
<i>a</i> , Å	12.516(2)	14.7625(18)	9.941(2)
<i>b</i> , Å	21.327(3)	12.220(2)	11.615(2)
<i>c</i> , Å	22.764(3)	33.672(5)	14.340(3)
α, deg	90	90	99.11(3)
β, deg	98.281(13)	90	103.27(3)
γ, deg	90	90	106.61(3)
<i>V</i> , Å ³	6012.8(16)	6074.6(16)	1499.1(5)
space group, <i>Z</i>	<i>Cc</i> , 4	<i>Pca</i> ₂₁ , 4	<i>P</i> $\bar{1}$, 1
ρ _{calcd} , g/cm ³	1.455	1.616	1.934
temp, K	130 ± 2	130 ± 2	130 ± 2
μ, mm ⁻¹	0.946	1.011	2.877
absorption correction transmission coeff			DIFFAST 1.000, 0.538
λ, Å	0.710 73	0.710 73	0.710 73
<i>R</i> indices	R1 ^a = 0.0742	R1 ^a = 0.1185	R1 ^a = 0.1178
[<i>I</i> > 2σ(<i>I</i>)]	wR2 ^b = 0.1834	wR2 ^b = 0.2137	wR2 ^b = 0.2540
<i>R</i> indices (for all data)	R1 ^a = 0.0980	R1 ^a = 0.2084	R1 ^a = 0.2453
	wR2 ^b = 0.2033	wR2 ^b = 0.2656	wR2 ^b = 0.3356

^a Based on *F*. ^b Based on *F*².

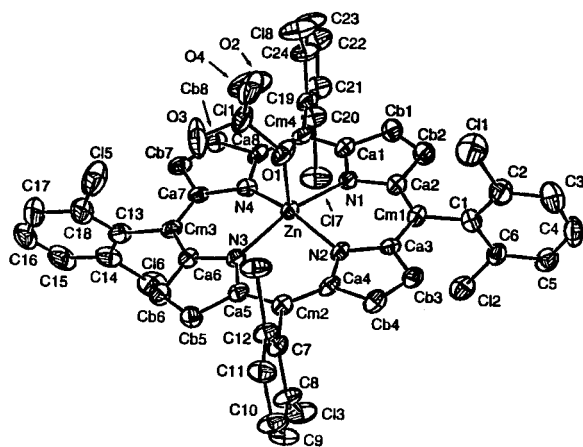


Figure 1. ORTEP diagram of the [Zn(TCl₂PP*)OCIO₃] π-cation radical showing the atom-labeling scheme. All ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

This particular porphyrin crystallizes with one chloroform molecule and one toluene molecule in the asymmetric unit. Due to the poor quality of this crystal, only the copper and chlorine atoms were refined anisotropically.

[Zn(TCl₂PPI₄)]·4THF. A violet thin plate of dimensions 0.14 × 0.10 × 0.01 mm was used. The triclinic crystal has one centrosymmetric porphyrin and four tetrahydrofuran molecules per cell with two THF molecules coordinated to the zinc atom.

Results

The molecular structure of [Zn(TCl₂PP*)OCIO₃] is shown in Figure 1. Figure 2 shows the displacements, in units of 0.01 Å, of the 24-atom porphyrinato core from the best least-squares plane. Values of the chemically unique bond distances (Å) are also displayed. The porphyrinato core displays a modest *C*_{4*v*} doming, and the molecules are well-separated. This conformation confirms the statement made by Scheidt and Lee⁵ that the saddle-shaped porphyrinato cores observed for several TPP π-cation derivatives is a result of dimerization. The zinc(II) atom is 0.40 Å out of plane (Figure 2). The dihedral angles of the four dichlorophenyl rings with the porphyrinato core are 86.8°,

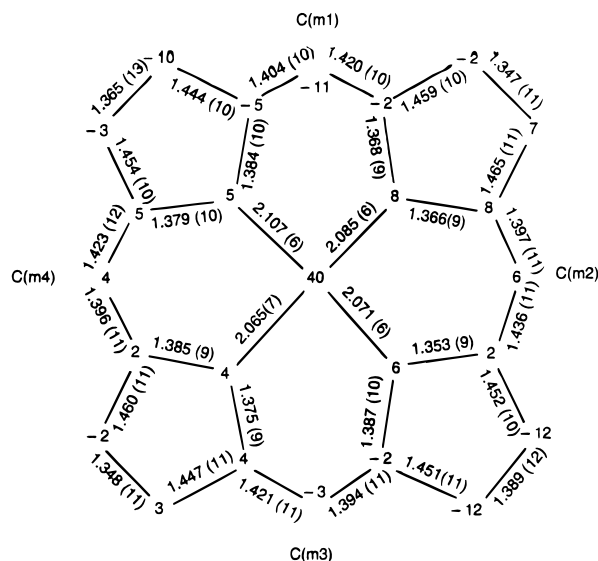


Figure 2. Formal diagram of the porphyrinato core of the [Zn(TCl₂PP*)OCIO₃] π-cation radical displaying the perpendicular displacement of the unique atoms (in units of 0.01 Å) from the mean plane of the 24-atom core. The bond distances (Å) in the core and coordination group are also displayed.

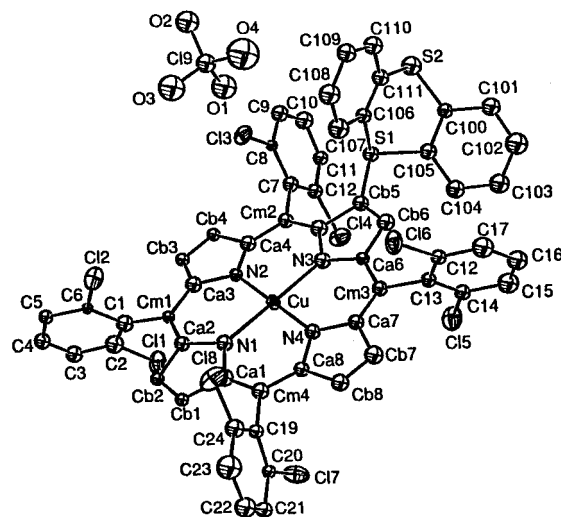


Figure 3. ORTEP drawing of the [Cu(TCl₂PPTTh)]ClO₄ molecule showing the atom-labeling scheme. All ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

74.4°, 86.1°, and 86.8°. The closest Zn...Zn separations are 11.86 and 12.36 Å, consistent with separated molecules. As for the [Cu(TMP*)][SbCl₆] π-cation radical,⁶ it can be seen that the bulky peripheral substituents prevent the π-π solid-state aggregation seen in the TPP derivatives. The eight *o*-chlorine atoms provide pockets on each side of the porphyrin plane. One pocket is occupied by the coordinated perchlorate and the other by the disordered hexane solvent molecule. The conformation of the porphyrinato core is not a result of any apparent intermolecular interactions.

An ORTEP drawing of [Cu(TCl₂PPTTh)]ClO₄·CHCl₃·C₆H₅-CH₃ including the numbering scheme is shown in Figure 3. The perpendicular displacements (in units of 0.01 Å) of the porphyrin core atoms from the 24-atom mean plane are shown in Figure 4. Values of the chemically unique bond distances (Å) are also displayed. The thianthrene substituent has a dramatic influence on the conformation of the porphyrinato core and leads to a saddle distortion of the macrocycle. The pyrrole bearing the thianthrene is also twisted relative to the mean plane of the porphyrinato core.

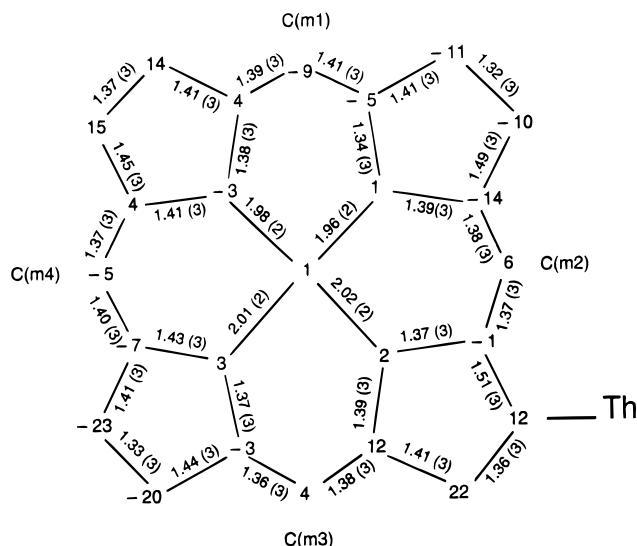


Figure 4. Formal diagram of the porphinato core of the $[\text{Cu}(\text{TCl}_2\text{-PPTH})]\text{ClO}_4$ molecule displaying the perpendicular displacement of the unique atoms (in units of 0.01 Å) from the mean plane of the 24-atom core. The bond distances (Å) in the core and coordination group are also displayed.

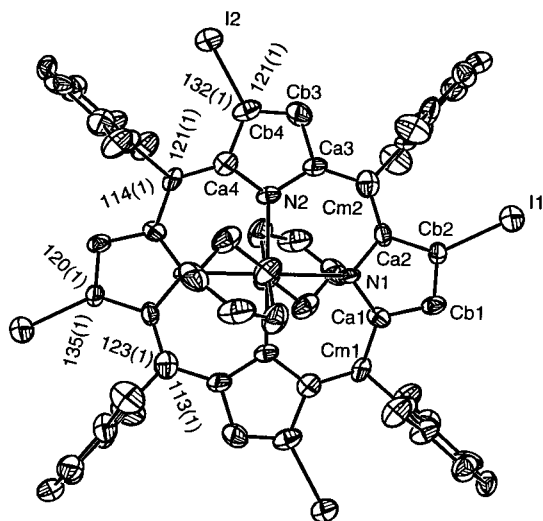


Figure 5. ORTEP drawing of the $[\text{Zn}(\text{TCl}_2\text{PPL}_4)(\text{THF})_2]$ molecule. The atom-labeling scheme is also displayed. All ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

The planes of the four dichlorophenyl rings are nearly perpendicular to the mean plane of the porphinato core (77° , 77° , 80° , 86°). The thianthrene substituent lies between the two peripheral phenyl groups which are the more tilted. The two phenylene rings linked by the two sulfur atoms make an angle of 52° .

Figure 5 is a drawing of the $[\text{Zn}(\text{TCl}_2\text{PPL}_4)(\text{THF})_2]$ molecule. In Figure 6 we see that the porphinato core is almost planar, with perpendicular displacements of atoms from the 24-atom core no larger than 0.05 Å. Like the two other structures described in this paper, the mean plane of the four dichlorophenyl groups are almost perpendicular to the mean plane of the porphinato core (89° and 85°).

Discussion

The reaction of $[\text{Zn}(\text{TCl}_2\text{PP})]$ with thianthrenium perchlorate afforded crystals of the π -cation radical, and the structure of the oxidized product has been obtained. The product has an IR band at 1262 cm^{-1} , comparable to that displayed by other meso-substituted π -cation radicals.^{21,22} The solvent and nonsolvent

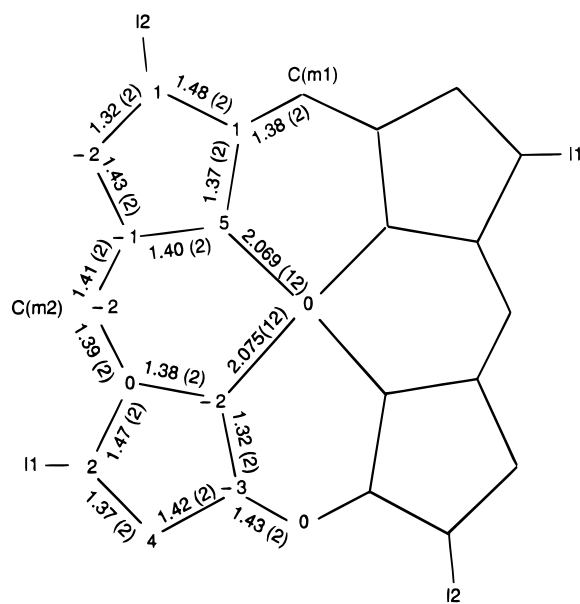


Figure 6. Formal diagram of the porphinato core of the $[\text{Zn}(\text{TCl}_2\text{-PPL}_4)]$ molecule displaying the perpendicular displacement of the unique atoms (in units of 0.01 Å) from the mean plane of the 24-atom core. The bond distances (Å) in the core and coordination group are also displayed.

used in the crystallization experiment, dichloromethane and *n*-hexane, are included in the structure. As expected, the species does not exhibit any intermolecular interactions in the solid state. The porphinato core displays a modest C_{4v} doming. Such doming is relatively rare in zinc derivatives and probably reflects the somewhat bulky nature of the dichlorophenyl groups. The dichlorophenyl groups are approximately perpendicular to the mean plane of the core. This feature is consistent with the observed EPR spectra described previously.¹³ The observed Zn–N_p distances range from 2.065(7) to 2.107(6) Å, and the Zn–O distance is 2.090(6) Å. These distances are similar to those found for derivatives of $[\text{Zn}(\text{TPP}^*)\text{OCIO}_3]$.^{3,4}

An examination of the bond distances of the 16-membered inner ring suggests that the expected short–long alternating pattern is present in $[\text{Zn}(\text{TCl}_2\text{PP}^*)\text{OCIO}_3]$. The averaged values for the expected short C_a–N bonds is 1.369(11) Å, while the expected long C_a–N bond distance average is 1.381(11) Å; the long and short values for the C_a–C_m distances are 1.425(13) and 1.398(12) Å, respectively. The numbers in parentheses are the estimated standard deviations calculated on the assumption that all averaged numbers were drawn from the same population. It is clear from the values of the estimated uncertainties that the pattern of interest is unfortunately observed at less than absolute statistical significance.

Figure 7 displays the expected long–short pattern. Figure 7 also displays observed values for the long and short distances in the 16-membered ring in five different porphyrin π -cation radical complexes where the pattern has been probably observed. The values for the four types of distances are (from top to bottom) those for the present $[\text{Zn}(\text{TCl}_2\text{PP}^*)\text{OCIO}_3]$ derivative, $[\text{Cu}(\text{OETPP}^*)]\text{ClO}_4$,²³ and the dimeric species $[\text{Zn}(\text{OEP}^*)\text{OH}_2]\text{-ClO}_4$,⁸ $[\text{Mg}(\text{OEP}^*)(\text{HOEt})][\text{Mg}(\text{OEP}^*)(\text{OCIO}_3)]\text{ClO}_4$,¹⁰ and $[\text{Fe}^{\text{III}}(\text{OEP}^*)(\text{Cl})]\text{ClO}_4$.⁹ The data from the present structure can be

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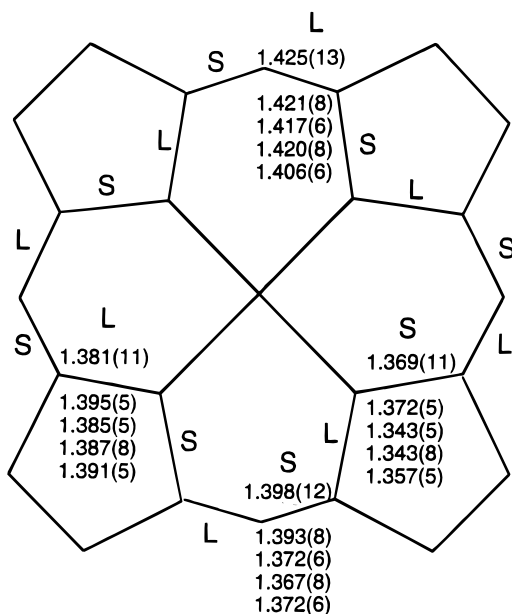


Figure 7. Formal diagram of a porphyrinato core showing the alternating long–short pattern in the 16-membered ring of porphyrins, from top to bottom, for $[\text{Zn}(\text{TCl}_2\text{PP}^*)\text{OClO}_3]$ (this paper), $[\text{Cu}(\text{OETPP}^*)]\text{ClO}_4$,²³ $[\text{Zn}(\text{OEP}^*)\text{OH}_2]\text{ClO}_4$,⁸ $[\text{Mg}(\text{OEP}^*)(\text{HOEt})][\text{Mg}(\text{OEP}^*)(\text{OClO}_3)]\text{ClO}_4$,¹⁰ and $[\text{Fe}(\text{III})(\text{OEP}^*)(\text{Cl})]\text{ClO}_4$.⁹ The symbols “S” and “L” show the pattern. The numbers in parentheses are the estimated standard deviations for the averaged values.

tentatively used to conclude that the alternating pattern can result from the mixing of the two states: A_{1u} and A_{2u} . The unfortunately limited precision for this structure is likely due to the presence of disordered *n*-hexane molecules in the crystalline lattice. We tried to grow other crystals of $[\text{Zn}(\text{TCl}_2\text{PP}^*)\text{OClO}_3]$ by using other nonsolvents in the liquid–liquid diffusion experiments; but, whatever the solvent selected, pentane, nonane, or cyclohexane, no new crystals were obtained.

We attempted to prepare the copper radical cation derivative by reaction of $[\text{Cu}(\text{TCl}_2\text{PP})]$ with thianthrenium perchlorate. Substantial difficulties were experienced in obtaining crystals for analysis. It was necessary to use a mixture of three solvents to grow even small crystals. To our surprise the crystal structure analysis showed that, instead of the expected π -cation radical, a new porphyrin derivative had been formed. The new product is a thianthrene adduct in which one β -pyrrolic hydrogen is substituted by thianthrene to form a sulfonium center. A perchlorate counteranion completes the structure, balancing the positive charge on the sulfur atom. The bulky thianthrene substituent has a strong influence on the conformation of the porphyrinato core leading to a modestly S_4 -saddled core. Although the very small size of the crystal limits the quality of the structure, the parameters are those expected for copper derivatives.²⁴

The formation of the thianthrene-substituted porphyrin derivative clearly requires a reaction between a porphyrinic and a thianthrenic reagent. The basic question is what might be concluded about the reacting species. Is the reacting species the neutral porphyrin or the porphyrin π -cation radical? It would be expected that these reactants would be coupled to the thianthrenium perchlorate radical or the neutral thianthrene, respectively. We have examined the reaction further to attempt to answer this question.

The UV–visible spectrum of the crystalline product equivalent to that used for the X-ray study consists of a Soret band at 433 nm and three visible bands at 524, 560, and 606 nm. This spectrum is distinctly different from that of the neutral copper, which has a Soret band at 415 nm and visible bands at 541 and 576 nm. Moreover, the spectrum of the cation radical has the typical blue-shifted Soret at 395 nm.²⁵ A CH_2Cl_2 solution containing 1 equiv of oxidant per copper porphyrin displays all three Soret bands that also have some time dependence; the band attributable to the radical cation diminishes while the 433 nm band increases. When the reaction was carried out in the presence of 3 equiv of oxidant per copper porphyrin, the relative proportion of these two bands increased substantially and followed the same time course. However, not all of the $[\text{Cu}(\text{TCl}_2\text{PP})]$ had reacted. A reaction in which 10 equiv of neutral thianthrene and 1 equiv of thianthrenium perchlorate was used had less original copper complex at the end. A reaction in which 10 equiv of thianthrene and 3 equiv of thianthrenium perchlorate was used gave a UV–visible spectrum that showed only a Soret band at 433 nm. Thin-layer chromatography on silica gel (made in a mixture of dichloromethane and methanol) showed a single spot. These results suggest that the porphyrin–thianthrene derivative is formed primarily, if not exclusively, by reaction between the porphyrin π -cation radical and the neutral thianthrene. This is in contrast to some reactions observed by Shine²⁶ in which the thianthrene radical is clearly the reactant leading to the sulfonium adduct. Reaction of porphyrin π -cation radicals to yield β -substituted products has been observed with triphenylphosphine²⁷ or pyridine²⁸ and (tetraphenylporphyrinato)iron(III) radical.

After this unusual result, we attempted reactions with another oxidant. Iodine and silver perchlorate have been used as an oxidant. For example, the system has been used in the $[(\text{FeTPP})_2\text{N}]$ oxidation.²⁹ The reaction of $[\text{Zn}(\text{TCl}_2\text{PP})]$ with $\text{AgClO}_4/\text{I}_2$ in THF led to a spectrum with a red shift of the Soret band and the α and β bands. Reaction with either iodine or silver perchlorate alone led to no observable change in the UV–visible spectrum. The red-shifted Soret suggests that the product (or products) is not a π -cation radical porphyrin but some other porphyrinic species.

Although the reaction system gives a mixture of products (vide infra), we were able to obtain crystals and determine the structure of one product. This product is indeed not a π -cation radical complex, but a tetraiodo derivative of a neutral porphyrin. Each pyrrole ring of the new porphyrin contains a single iodine atom on a β -carbon atom. The four iodine atoms are at the symmetric β -pyrrole positions 2, 7, 12, 17 (cf. Figure 5). This appears to be an unusual substituent pattern. The related tetrabromotetraphenyl has substituents on only two pyrroles, i.e., at the 2,3 and 12,13 positions.³⁰ Very little information is available on iodinated porphyrins. Unsuccessful attempts with *meso*-tetraphenylporphyrin have been published; these used iodine and acetic acid³¹ or *N*-iodosuccinimide.³² In 1990, a

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(25) It appears that the copper complex is more difficult to oxidize than the zinc complex. For example, we did not ever obtain a spectrum with a single Soret that could be attributed to a solution of the pure radical when thianthrenium perchlorate was used as the oxidant.

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moniodo derivative of deuterioporphyrin III dimethyl ester and a diiodo derivative of deuterioporphyrin IX dimethyl ester were prepared with iodine in *o*-dichlorobenzene.³³

Halogenation by molecular halogen is a classical organic reaction. For iodination reactions, it is well-known that the reactive species is the cation I^+ .³⁴ Here, this cation appears to be provided by reaction of I_2 with silver perchlorate.³⁵ Note that AgI and not a silver mirror is a product of the reaction. The symmetric tetraiodoporphyrin product is not the only product of the reaction. Although chromatography on silica gel columns gave only a single band, the 1H NMR spectrum is not compatible with a single β -substituted species. We suspect that the other species are other iodination products, most probably the mono-, di-, and triiodo species. Isomeric tetraiodides may also be present. Attempts to purify the iodination product by chromatography of the demetalated product were also unsuccessful. The $AgClO_4/I_2$ reaction also appears to iodinate the copper derivative, but the reaction was not studied in detail.

The iodination of the porphyrin derivative $[Zn(TCl_2PP)]$ was carried out in THF solution and crystals obtained from THF solution. Thus the fact that the crystalline material isolated was the molecule $[Zn(TCl_2PPI_4)(THF)_2]$ is not surprising. The metrics of the zinc coordination group of this complex are similar to those reported for a related species $[Zn(TPP)(THF)_2]$.³⁶

The presence of β -chloro or -bromo substituents in *meso*-tetraarylporphyrin leads to peripherally crowded porphyrin derivatives. The structures of a number of such derivatives have been determined and are frequently found to have nonplanar (saddled) conformations.^{30,37} This is not seen in the present

tetraiodo derivative, where the largest deviation from planarity of the 24-atom core is 0.05 Å (cf. Figure 6). Nonetheless, the iodine atoms are close to the dichlorophenyl rings. The interatomic distances between the iodine atoms and the carbon atoms of the closest dichlorophenyl range from 3.33 to 4.33 Å for both independent iodides. The sum of the van der Waals radii for an iodide atom and an aromatic carbon atom is ~ 3.85 Å (2.15 + 1.70). This leads to some significant adjustments to accommodate the two close, large groups. Figure 5 displays the bond angles around the meso carbon atoms and the substituted β carbon atoms. The deviations from symmetric bond angles involving both serve to increase the separations between the two groups.

The chemistry and structures of the three complexes of 5-, 10,15,20-tetra(2,6-dichlorophenyl)porphyrin derivatives reported herein show that the species have unusual properties including reactivity at the β -positions.

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Supporting Information Available: Tables S1–S18, listing complete crystallographic details, atomic coordinates, anisotropic temperature factors, fixed hydrogen atom positions, and complete listings of bond distances and angles for $[Zn(TCl_2PP^*)OCIO_3]$, $[Cu(TCl_2PPTTh)]ClO_4$, and $[Zn(TCl_2PPI_4)]$ structures. A file containing crystallographic data collection and refinement data, atomic coordinates, thermal parameters, bond distances, and bond angles, in CIF format, is also available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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