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Synthesis and Structural Determination of a Porphyrinatoplatinum(II): *meso*-Tetrakis(4-*t*-butylphenyl)porphyrinatoplatinum(II)

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A substituted porphyrinatoplatinum(II), *meso*-tetrakis(4-*t*-butylphenyl)porphyrinatoplatinum(II), has been spectroscopically and structurally characterized. The ^{1}H NMR signal from the β-protons of the pyrrole ring is observed as a singlet with a full-width at half maximum of 1.6 Hz, contrary to the reported quasi-triplet resonance attributable to the ^{1}H–^{195}Pt long-range coupling. The porphyrin nucleus is nearly planar in the solid state. All macrocycle atoms lie within approximately 0.06 Å of the least squares mean plane with a *pseudo*-wave core conformation. The intramolecular Pt–N distances are 2.019(3) Å.

Platinum(II) porphyrin ($Pt^{II}Por$) has been attracting a lot of attention from the viewpoint of coordination chemistry.[1] The large metal-to-porphyrin π-bond confers specific properties to this metal complex,[2,3] e.g., the electrophilic behavior of the porphyrinato ligand[1,4] and the metal-centered redox reaction.[1,5] Additionally, a closed-shell low-spin d^8-configuration and a large spin–orbit interaction associated with the large atomic weight of platinum produce red phosphorescence at room temperature at approximately 630 nm.[6] This specific character has led to the discovery of the electroluminescent (EL) properties of 2,3,7,8,12,13,17,18-octaethylporphyrinatoplatinum(II) ($Pt^{II}OEP$) by two independent groups,[7] Forrest and co-workers in 1998[8] and Friend and co-workers in 1999.[9] Combined with green (G) and blue (B) light emitting dyes, the red (R) light of $Pt^{II}Por$ is expected to be used in full-color RGB EL displays.[7d] Furthermore, the long triplet life time and the luminescence from this spin state make $Pt^{II}Por$ compounds suitable for use as triplet sensitizers[10] and as oxygen sensors.[11] These findings confirm that $Pt^{II}Por$ is a key component molecule for contemporary interdisciplinary advanced material chemistry.

In addition, it should be interesting to discuss the relationship between the distortion of the porphyrin nucleus and the nature of the incorporated metal, particularly group-10 metals such as nickel, palladium, and platinum. Studies on the corresponding nickel(II) complexes have been conducted in order to mimic and/or to elucidate the function of *Factor-430*, a key component of the active site of methylcoenzyme M-reductase, which catalyzes the final chemical step of methane formation by methanogenic organisms.[12] Presently, it is postulated for this specific redox reaction that a small ionic radius of divalent four-square-coordinated nickel(II) induces the Ni(I)/Ni(II) redox couple accompanying the large conformational distortion of the ligand.[13]

To understand the unique functions of $Pt^{II}Por$ described above, a discussion based on the structure of $Pt^{II}Por$ seems essential. However, to our surprise, $Pt^{II}Pors$ with well-characterized structures are limited only to *meso*-tetraphenylporphyrinatoplatinum(II) ($Pt^{II}TPP$)[14] and $Pt^{II}OEP$[15] (Chart 1). Because the planarity of the porphyrin nucleus of these two complexes was reported to be ruffled for the former and planar for the latter, the nature of the $Pt^{II}Por$ complex remains unclear and confusing. With this information in mind, we performed a structural determination of a platinum(II) porphyrin derivative, *meso*-tetrakis(4-*t*-butylphenyl)porphyrinatoplatinum(II) ($PtT4^{t}BuPP$), the corresponding free base ($H_2T4^{t}BuPP$), and the metal complexes of which are widely used[16–22] because of their enhanced solubilities in usual organic solvents, attributable to the four *t*-butyl groups. In this study, our goal is to investigate this class of materials further.

Experimental

General. Pyrrole (TCI), 4-*t*-butylbenzaldehyde (TCI), propionic acid (Kishida Chemical Co., Ltd.), and platinum(II) chloride (Kojima Chemical Co., Ltd.; purity >99%) were used as received. Infrared spectra were recorded on a Shimadzu FTIR-8400 instrument using the KBr pellet technique in the range of 650 to 4000 cm^{-1}. Absorption spectra were recorded on a Hitachi U-3500. Laser desorption/ionization time-of-flight mass spectra were recorded on a Kratos Analytical KOMPACT PROBE. Thermal properties were studied on a Rigaku TG-8120 thermogravimetric analyzer. TGA was performed using freshly prepared PhCl solvated crystal filtered from PhCl and dried under ambient conditions for 30 min. Samples were placed in an aluminum pan and heated to 450 °C at 15 °C min^{-1} under a continuous flow of nitrogen (10 mL min^{-1}).

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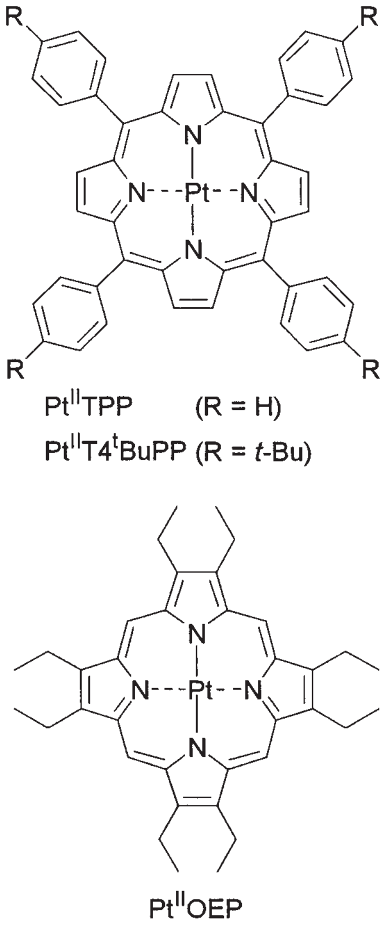

Chart 1.

meso**-Tetrakis(4-*****t*****-butylphenyl)porphyrin (H$_2$T4^{t}BuPP).** This free base[23] was prepared according to the reported method[24] using pyrrole, 4-*t*-butylbenzaldehyde, and propionic acid. ^{1}H NMR (CDCl$_3$) δ 8.87 (s, 8H), 8.15 (d, $J = 8.2$ Hz, 8H), 7.76 (d, $J = 8.2$ Hz, 8H), 1.61 (s, 36H), and -2.75 (bs, 2H). IR (KBr) 3315, 1475, 993, 982, 968, and 802 cm^{-1}. UV–vis (CHCl$_3$) λ (log ε) 421 (5.54), 516 (4.16), 551 (3.92), 593 (3.66), and 651 (3.63) nm.

meso**-Tetrakis(4-*****t*****-butylphenyl)porphyrinatoplatinum(II) (Pt^{II}T4^{t}BuPP).** 515 mg of H$_2$T4^{t}BuPP (0.61 mmol) and 816 mg of PtCl$_2$ (3.1 mmol, 5 eq.) were dissolved in 30 mL of freshly distilled benzonitrile. The mixture was purged with nitrogen and refluxed for 2 h. The solvent was removed under reduced pressure. The residue was extracted with CHCl$_3$ and filtered through a Celite® pad. The filtrate was concentrated to approximately 20 mL and subjected to silica-gel chromatography eluted by CHCl$_3$. The most rapidly eluted orange band was collected. The solvent was concentrated to about 50 mL under reduced pressure and 50 mL of MeOH was added to obtaine 627 mg of the product (quant.). ^{1}H NMR (CDCl$_3$) δ 8.78 (s, 8H), 8.07 (d, $J = 8.2$ Hz, 8H), 7.73 (d, $J = 8.2$ Hz, 8H), and 1.59 (s, 36H). IR (KBr) 1369, 1015, 814, and 797 cm^{-1}. UV–vis (CHCl$_3$) λ (log ε) 404 (5.41), 510 (4.39), and 538 (3.66) nm.

X-ray Experiment. A single crystal of Pt^{II}T4^{t}BuPP suitable for diffraction study was isolated from chlorobenzene–MeOH mixed solvent. The crystal data of the complexes are summarized in Table 1. The temperature was calibrated with an Anritsu HFT-50 thermometer. Data for the complex was collected on a Rigaku AFC7R four-circled diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71070$ Å, 50 kV, 200 mA) equipped with a Rigaku low-temperature device. The data were collected using the ω–2θ scan technique to a maximum 2θ value of 55°. Neutral atom scattering factors were taken from Cromer and Waber.[25] Anomalous dispersion effects were included in F_{calc};[26] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[27] The values for the mass attenuation coefficient are those of Creagh and Hubbel.[28] All calculations were performed using the teXsan[29] crystallographic software package of Molecular Structure Corporation.

Table 1. Crystal Data and Structure Refinement Parameters for [Pt^{II}T4^{t}BuPP]•PhCl

Identification code	[Pt^{II}T4^{t}BuPP]•PhCl
Formula	$C_{66}H_{65}ClN_4Pt$
Formula weight/g mol^{-1}	1144.81
Temperature/K	182
Crystal system	monoclinic
Space group	$P2_1/n$ (#14)
a/Å	22.603(5)
b/Å	9.679(2)
c/Å	24.084(4)
β/°	91.80(2)
Cell volume/Å^3	5266(1)
Z	4
Crystal size/mm	0.50 × 0.33 × 0.08
D_{calc}/Mg m^{-3}	1.444
Wavelength/Å	0.71069
Absorption coefficient/mm^{-1}	27.51
$R1$	0.036
$R1$ for all data	0.060
Crystallization solvent	Chlorobenzene/MeOH

Results and Discussion

Synthesis. The free base porphyrin, H$_2$T4^{t}BuPP,[23] was prepared under the usual Adler–Long reaction conditions using commercially available 4-*t*-butylbenzaldehyde.[24] The metallation reaction was performed by using platinum(II) chloride (Pt^{II}Cl$_2$) in boiling benzonitrile[30] to give orange Pt^{II}T4^{t}BuPP in quantitative yield. Laser desorption time-of-flight mass spectroscopic data clearly support the obtained compound to be Pt^{II}T4^{t}BuPP.

It was pointed out by Milgrom that the ^{1}H NMR peak of the β-protons of Pt^{II}Pors is comprised of three peaks with 1:4:1 relative intensity, i.e., the central main peak attributable to the complexes containing ^{194}Pt or ^{196}Pt (both $I = 0$) is flanked by two satellite peaks about 6–8 Hz away on either side of it.[31] The satellite peaks are attributable to the long-range ^{1}H–^{195}Pt ($I = 1/2$) coupling. However, in our study, the peak attributable to the β-protons was observed as a singlet with a full-width at half maximum of 1.6 Hz (vide infra). Other signals attributable to the attached phenyl groups, 8.07 (*ortho*-H) and 7.73 (*meta*-H) ppm, are in the range observed for the TPPs.[31]

In the IR spectra, the absorption at 3315 cm^{-1}, attributable to N–H stretching for H$_2$T4^{t}BuPP, was not observed for Pt^{II}T4^{t}BuPP. The well-resolved C–H rocking vibrations of the pyrrole ring of H$_2$T4^{t}BuPP, 993, 982, and 968 cm^{-1}, changed to a strong singlet at 1015 cm^{-1} after the metallation, consistent with the previously reported IR spectra of PtTPP.[2] The vibration at 1475 cm^{-1}, indicating the –C=N– stretching vibration of the free base, also shifted to 1360 cm^{-1} after the metallation.

This Pt$^{\rm II}$Por, in which four phenyl groups are attached perpendicularly to the porphyrin nucleus, also acts as a "*porphyrin sponge*" by incorporating one chlorobenzene (PhCl) molecule, as characterized by the single-crystal diffraction study (vide infra).[32] This finding is in marked contrast to that of a structurally similar Pt$^{\rm II}$TPP forming a non-solvated crystal.[14] Thermogravimetric analysis (TGA) showed that the weight loss started at room temperature, indicating that the PhCl is loosely incorporated in the crystal lattice (vide infra). A steady weight loss was observed below 153 °C.

Structure. The structure contains one crystallographically independent porphyrin molecule and one PhCl molecule. The crystal structure of Pt$^{\rm II}$T4^{t}BuPP is shown in Fig. 1 and some important structural parameters of the complex are summarized in Table 2 together with the data of reference complexes including Pt$^{\rm II}$TPP[14] and Pt$^{\rm II}$OEP,[15] as well as other typical metalloporphyrins incorporating group-10 metals.

One of the most important structural parameters that best characterizes the complex is the average metal–nitrogen bond distance ($d_{\rm M-N}$) of 2.019(3) Å for Pt$^{\rm II}$T4^{t}BuPP, which is comparable to that reported for Pt$^{\rm II}$OEP (2.012(3) Å),[14] and slightly larger than that for Pt$^{\rm II}$TPP (2.008(2) Å)[15] and the value of 2.010 Å for the ideal reference metalloporphyrin with the least strain.[33] Furthermore, this distance is much larger than the typical value of 1.96 Å for nickel derivatives with a planar nucleus,[34] and slightly smaller than that for porphyrinatopalladiums (2.014 Å).[35] The order of the average $d_{\rm M-N}$s for d^8-metalloporphyrins, 1.96 Å (for Ni) < 2.013 Å (for Pt) ≤ 2.014 Å (for Pd), may be related to the order of the mean ionic radius for four square-planar d^8-metals, i.e., 0.63 Å (for Ni) < 0.74 Å (for Pt) < 0.78 Å (for Pd).[36]

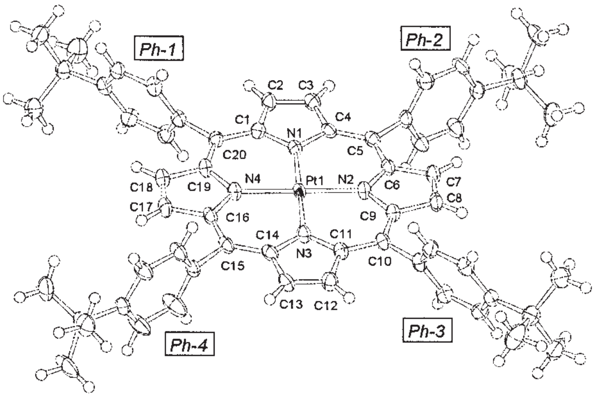

Fig. 1. ORTEP drawings of Pt$^{\rm II}$T4^{t}BuPP. Thermal ellipsoids are 50% probability levels.

Table 2. Comparison of Important Structural Parameters of Pt$^{\rm II}$T4^{t}BuPP with Those of Related Compounds

	$d_{\rm M-N}$/Å	Δ/Å[a)]	Reference
Pt$^{\rm II}$T4^{t}BuPP	2.019(3)	0.027	(this work)
Pt$^{\rm II}$TPP	2.008(2)	0.226	14
Pt$^{\rm II}$OEP	2.012(3)	0.009	15
Pd$^{\rm II}$TPP	2.009(9)	0.226	30a
Pd$^{\rm II}$OEP	2.014(3)	0.014	30b
Ni$^{\rm II}$TPP	1.931(2)	0.264	41
Ni$^{\rm II}$OEP (triclinic-A)	1.958(2)	0.018	42
Ni$^{\rm II}$OEP (triclinic-B)	1.952(8)	0.029	43
Ni$^{\rm II}$OEP (tetragonal)	1.929(3)	0.298	44

a) The root-mean-square out-of-plane displacement of the 24 atoms (see Ref. 34 and 39).

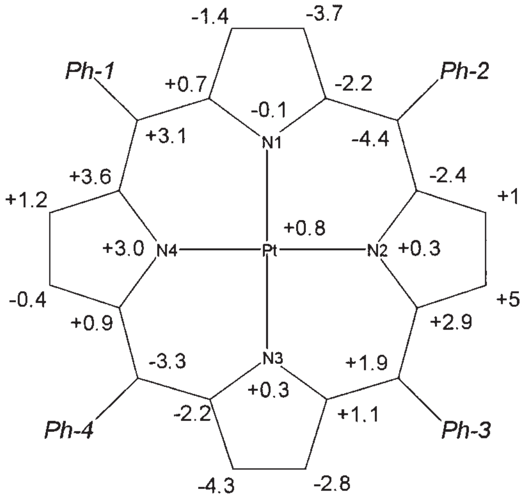

Fig. 2. Formal diagram of the macrocycle of Pt$^{\rm II}$T4^{t}BuPP. The out-of-plane displacements (in units of 0.01 Å) of each atom from the 24-atom mean plane are shown.

From Figs. 1 and 2, it is clear that Pt$^{\rm II}$T4^{t}BuPP is nearly planar in the solid state. All macrocycle atoms lie within approximately 0.06 Å of the least squares mean plane (Fig. 2). Smith and co-workers classified the distortions of the porphyrin nucleus into four types: *saddle*, *wave*, *ruffle*, and *dome*.[37] Pt$^{\rm II}$T4^{t}BuPP is considered to have the *pseudo-wave* core conformation, in which the line through C(9)–Pt(1)–C(19) acts as an edge and/or trough of the wave.

A mean plane was fitted to the 24 atoms of the porphyrin nucleus defined according to Schomaker and his co-workers.[38] The root-mean-square out-of-plane displacement of the 24-atom macrocycle (Δ)[34,39] is 0.027 Å. Although this value is larger than that for Pt$^{\rm II}$OEP (0.009 Å), a molecule that is closely packed due to strong π–π interactions, Pt$^{\rm II}$T4^{t}BuPP is more planar than the structurally similar Pt$^{\rm II}$TPP. The deformation of the latter complex is considered to be a result of packing forces. It is well known that the deformation of the porphyrin nucleus decreases the $d_{\rm M-N}$ bond distances of Ni$^{\rm II}$Por systems.[33] Although only three crystal structures exist, including that of the present study, a similar tendency is also observed for Pt$^{\rm II}$Por systems.

The dihedral angles between the porphyrin plane and the aryl groups are 75.5(1)°, 87.9(1)°, 72.6(1)°, and 86.3(1)° for *Ph-1*, *Ph-2*, *Ph-3*, and *Ph-4*, respectively (Fig. 1). These values are within the range of those observed for the other TPPs.[40]

The packing structure of Pt$^{\rm II}$T4^{t}BuPP is shown in Fig. 3. Each *t*-butyl group contacts the *t*-butyl group of the adjacent Pt$^{\rm II}$T4^{t}BuPP. This attractive van der Waals attractive force produces the two-dimensional perfect sheet structure in the *ac*-plane. In the sheet, molecules pack like a window mill. The solvent molecule, PhCl, is incorporated in the space between two molecules. No short atomic contacts exist between PhCl and Pt$^{\rm II}$T4^{t}BuPP. This is the main reason why the solvent

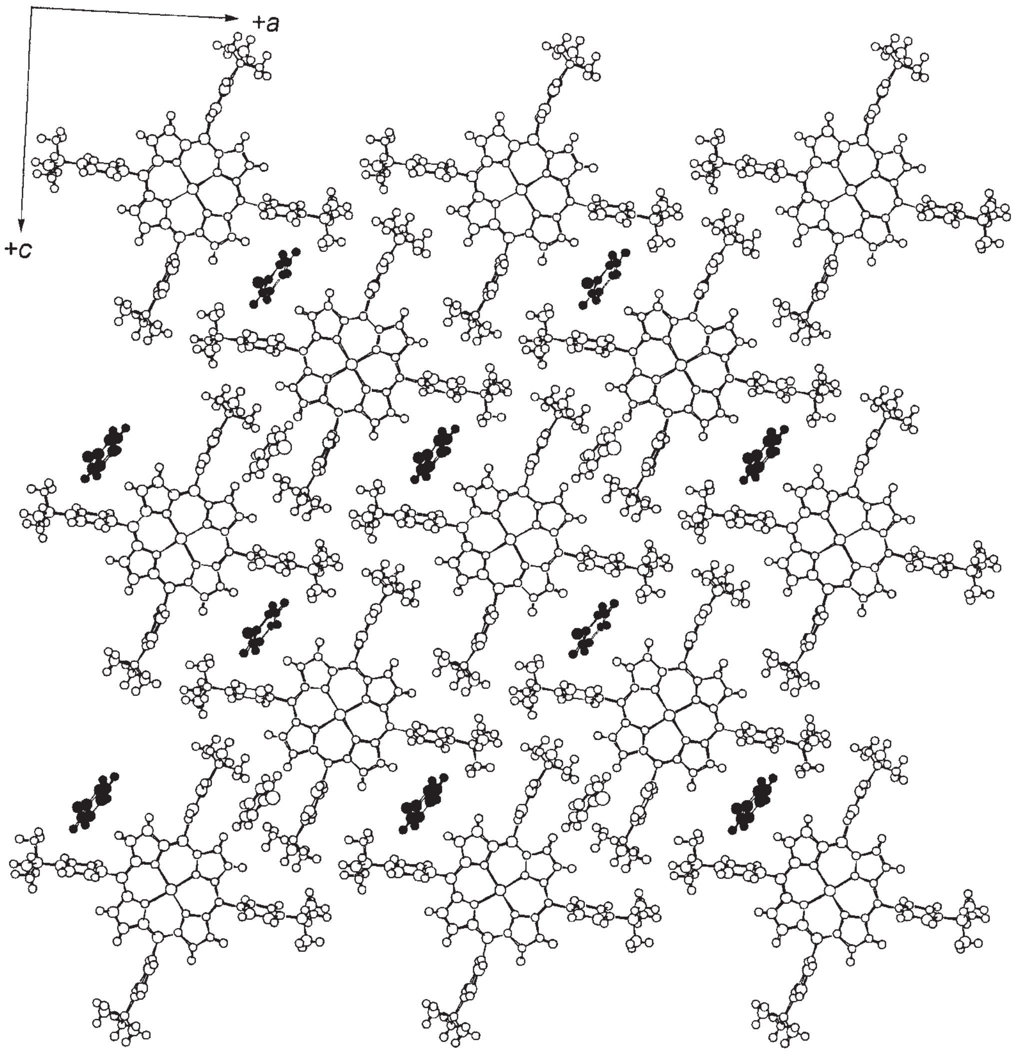

Fig. 3. Top view of the crystal packing of $Pt^{II}T4^{t}BuPP$. Solvent molecules, chlorobenzene, are shown by dark circles.

molecule is weakly incorporated in the crystal, evaporating even at room temperature. This sheet is stacked in the *b*-direction with an interplanar distance of 4.84 Å (= $b/2$).

Conclusions

A substituted platinum(II) porphyrin was structurally and spectroscopically characterized. Two paramount conclusions can be drawn from our investigation.

First, the ^1H NMR signal of the β-hydrogen atoms of the porphyrin nucleus was a sharp singlet at 8.78 ppm. This is in marked contrast to the previously observed *quasi*-triplet resonance.[31] It is well known that the spin coupling constant mainly depends on the dihedral angle between the atoms, i.e., the spin coupling constant provides information about the conformation of the molecule. Hence, the different observations described above might result from the conformational differences among the $Pt^{II}Pors$. Although the dihedral angle dependent coupling constant of the metalloporphyrin system is not known, our findings may suggest a new methodology to estimate the planarity of the porphyrin nucleus using long-range spin coupling between ^{195}Pt and β-protons, along with frequently used Raman spectroscopy[34] and single-crystal diffraction methods.[37]

Second, the crystal structure provided herein is, to our knowledge, the third one of $Pt^{II}Pors$. The core deformation of $Pt^{II}T4^{t}BuPP$ was estimated from the Δ-value,[34,39] and is between those of $Pt^{II}OEP$ and $Pt^{II}TPP$ (Table 2). The "*true*" conformation of $Pt^{II}Por$ is still unclear, i.e., whether planar or bent. Our results suggest that platinum can also induce flexible core conformations, as observed for porphyrinatonickels.[41–44] This suggests the potential utility of $Pt^{II}Pors$ in estimating the biological function of *Factor-430* using its strong luminescent character, the possibility of detecting unknown reduced $[Pt^{I}Por]^-$ and $[Pt^{0}Por]^{2-}$ species, and the creation of an artificial enzyme based on $Pt^{II}Pors$.

Because of the enhanced solubility in standard organic solvents and the well-characterized structural information provided by this work, $Pt^{II}T4^{t}BuPP$ is expected to be widely used as a standard compound in the field of $Pt^{II}Por$ chemistry. We are currently working on further modifications of the porphyrinato ligand and its excited state chemistry.

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$$\Delta = \sqrt{\sum_{i=1}^{24} \frac{{\delta_i}^2}{24}},$$

where δ_i is the orthogonal displacement of the macrocycle atom i from the mean plane. The sum includes all 24 atoms of the porphyrin macrocycle.

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