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Metalloporphines: Dimers and Trimers

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Abstract

Procedures for the purification and subsequent crystallization of the slightly soluble four-coordinate metalloporphines, the simplest possible porphyrin derivatives, are described. Crystals of the porphine derivatives of cobalt(II), copper(II), platinum(II) and two polymorphs of zinc(II) were obtained. Analysis of the crystal and molecular structures show that all except the platinum(II) derivative form an unusual trimeric species in the solid state. The isomorphous cobalt(II), copper(II), and one zinc(II) polymorph pack in the unit cell to form dimers as well as the trimers. Interplanar spacings between porphine rings are similar in both the dimers and trimers and range between 3.24 and 3.37 Å. Porphine rings are strongly overlapped with lateral shifts between ring centers in both the dimers and trimers with values between 1.52 to 1.70 Å or in Category S as originally defined by Scheidt and Lee. Periodic trends in the M–N_p bond distances parallel those observed previously for tetraphenyl- and octaethylporphyrin derivatives.

Graphical abstract

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Notes

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Supporting Information Available: Figures S1–S10 provide ORTEP diagrams for [Cu-(porphine)], [Pt-(porphine)] and two forms of [Zn(porphine)] (10 pages). Crystallographic information files (CIF) are also available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Portion of the unit cell of Co(porphine) displaying the concurrent appearance of both dimer and trimer interactions in the simplest porphyrin molecules.

Introduction

The importance of metalloporphyrins is very wide-ranging and extends to energy conversion, cytochromes, heme proteins, the photosynthetic reaction center including the special pair, geochemistry, and catalysis.¹ Porphyrin core conformational aspects, originally reviewed by Scheidt and Lee,² have been suggested to have significant influences on a number of properties, including redox potentials,^{3, 4} axial ligation,⁵ electron transfer rates,^{5, 6} and photophysical processes.^{7–9} Core conformations of metalloporphyrins are known to be influenced by peripheral substituents and by the size of the central metal ion. Bulky peripheral groups lead to nonplanar configurations including both ruffling and saddling, whereas small metal ions leads primarily to ruffling distortions.

Although the synthesis of the unsubstituted molecule porphine (also called porphyrin) has long been known,^{10–12} the yields were impracticably small for systematic studies. A more recent synthesis with much improved yields is now available¹³ that yields sufficient quantities to explore the coordination chemistry of porphine. However, the limited solubility of the porphine derivatives has also long hindered characterization including molecular structure determinations. We now report what seems to be a general and useful way of purifying and crystallizing these derivatives. With this procedure we have prepared crystalline material for the cobalt(II), copper(II), zinc(II), and platinum(II) derivatives and report their crystal and molecular structures.

In this report we explore the general nature of a number of metalloporphine derivatives. Porphine, the simplest possible porphyrin, has no peripheral substituents. We examine the core conformations with several metal ions to consider possible effects of the metal ion size.

Experimental Section

Materials and Crystals

The metalloporphine derivatives [Zn(porphine)], [Cu(porphine)], [Co(porphine)], and [Pt(porphine)] were purchased from Porphyrin Products (Frontier Scientific) and were purified by liquid column chromatography using carbon disulfide (CS₂) as the mobile phase

(column $1 \times 10 \text{ cm}^2$; Silica 32–63, 60 Å, ICN Biomedicals). The integrity of the samples was monitored by thin-layer chromatography using Kieselgel with the fluorescence indicator F254 (Merck) and CS_2 as solvent. All solvents used were HPLC grade (Aldrich). Single crystals of the porphine derivatives was grown by very slow evaporation from CS_2 solution. After approximately 5 months, plate-shaped crystals of each derivative were obtained. X-ray sized crystals was cleaved and used for X-ray diffraction; all specimens were thin plates with dimensions given in the Supporting Information (CIF files).

Structural Analysis

Crystals of all five metalloporphine derivatives were examined on an Enraf-Nonius FAST area detector diffractometer at 130 K using methods and procedures described earlier.¹⁴ A brief summary of the determined cell parameters and data refinements results are given in Table 1; more complete details are given in the CIF files found in the Supporting Information. Reflection data were reduced using Lorentz-polarization factors and were corrected for the effects of absorption. Positional parameters for the two crystalline forms of [Zn(porphine)] and that for [Pt(porphine)] were obtained from the direct methods program SHELXS, whereas those for [Co(porphine)] and [Cu(porphine)] were obtained from the isomorphous zinc complex. Ensuing difference Fourier maps revealed all hydrogen atoms, which were included in the final refinement as idealized riding atoms ($\text{C-H} = 0.95 \text{ Å}$). Positional parameters were refined to convergence along with their anisotropic displacement parameters. All reflections, including those with negative intensities, were included in the refinement and the $I \geq 2.0\sigma(I)$ criterion was used only for calculating R_1 .¹⁵

Results and Discussion

Crystal structures of the simplest porphyrin derivatives, those of porphine, have been limited by the lack of crystals that results from the relatively low solubility of the compounds. However, as described in the experimental, careful purification followed by slow evaporation from carbon disulfide solution, provides a generally useful method of crystallization. Accordingly, the crystal and molecular structure of five new metalloporphine derivatives have now been determined. These include Pt(II), Co(II), Cu(II) derivatives, and two Zn(II) polymorphs. In all five structures, the crystalline lattice contains only the metalloporphine molecules; no solvent molecules of crystallization are present.

An unexpected feature of the crystal structures of all derivatives except that of the platinum species is the inter-ring interactions. In the four other derivatives, the intermolecular interactions between the planar molecules are not simply those of dimeric species but also involve the formation of trimeric species as well. The usual forms of intermolecular interactions in planar metalloporphyrins is either dimeric interactions or that of extended linear stacks.² The observation of discrete trimeric species is thus unusual. A summary of the intermolecular interactions of all five species plus that of the previously described [Ni(porphine)]¹⁶ is given in Table 2.

Dimeric interactions have been observed in the solid state structure of the free base¹⁷ and in the recently described vanadyl derivative.¹⁸ A report of the five-coordinate zinc(II) complex [Zn(porphine)(Py)] does not display dimeric interactions, but an entirely different packing

motif.¹⁹ An interesting inclusion complex reported by Fujita and coworkers has a dimeric pair of free base porphines.²⁰ In all of these dimeric species, the inter-ring metrics are similar to the dimeric species reported herein.

The interplanar interactions given in Table 2 can be described quantitatively by three values: the mean plane separation (M.P.S), the lateral shift of the two rings (L.S.) and the ring center to ring center (Ct...Ct) distance. This is illustrated in Figure 1. Although the diagram shows the interaction between two rings, this scheme can clearly be also applied to the interactions between ring pairs of a trimer. The nearly constant perpendicular ring...ring separation of 3.230–3.369 Å is consistent with the inter-ring π – π interactions driving the dimer and trimer interactions.

Side-on and top-down views of the dimeric and trimeric ensembles found for [Co(porphine)] are given in Figures 2 and 3. The two sets of diagrams illustrate the symmetry operations relating the rings of the dimers and the trimers. In all dimeric structures described in this manuscript, the two rings are related by an inversion center between the two rings. Accordingly, the two rings are precisely parallel and the M–N_p bonds of the two rings are also required to be parallel. In the trimeric ensembles, the center porphine ring of the three has inversion symmetry, thus relating the two outer rings. Again the two outer rings are required to be precisely parallel to each other and the center ring is also effectively parallel to the two outer rings. The M–N_p bonds are also all parallel to each other in the trimer although this is required only for the outer pair of porphine rings. These diagrams adequately illustrate the dimers and trimers of all other species described in this paper and equivalent illustrations for [Cu(porphine)] (dimer and trimer), [Zn(porphine)]#1 (dimer and trimer), [Pt(porphine)] (dimer only), and [Zn(porphine)]#2 (trimer only) are given in the Supporting Information.

Four of the five metalloporphine species reported herein form trimeric species as shown in Figures 2 and 3 and in the Supporting Information figures. The porphine rings are not precisely flat, but however display only modest deviations from exact planarity. The central ring of the trimers shows a very modest stepped² or waved²¹ conformation, while the outer rings of all trimers display a small ring ruffling. The outer cores of one zinc(II) derivative (#2) also shows a modest doming contribution as well as ruffling.

Dimeric species are found in the crystal lattices for four of the derivatives. The core conformation for the cobalt(II), copper(II), and platinum(II) derivatives display very modestly ruffled cores, while a zinc(II) derivative (#1) shows a modest component of doming as well. The zinc atoms in both the dimers and trimers display a modest (~0.15 Å) out-of-plane displacement towards the center of the units. In all other derivatives, the metal is essentially at the center of the rings. Mean plane diagrams for [Co(porphine)] are given in Figure 4 and equivalent figures for the remaining derivatives are found in the Supporting Information.

The mean plane diagrams also report the averaged values of bond distances and bond angles for each ring. The structural patterns within the rings of these simplest porphine species are found to be comparable to those found earlier for the corresponding derivatives with varying

peripheral substituents. As has long been recognized, the core conformation can have a substantial effect on the M–N_p distances,²² with significant differences for planar and ruffled cores. Accordingly, we take note of core conformations in our comparisons.

The average Co–N_p distance in the dimer and trimer (10 unique distances) is 1.973 (3) Å. This value is consistent with a low-spin state for cobalt(II) (electron configuration (d_{xy}, d_{xz}, d_{yz})⁶(d_z)¹). This value is that expected for planar derivatives and can be compared with [Co(OEP)] (1.971 Å)^{14, 23} and two planar fluorinated tetraphenylporphyrin derivatives (1.976 Å for TF₅PP and 1.971 Å for T(p-Me₂N)F₄PP).²⁴ There are two nonplanar forms of [Co(TPP)], a ruffled form (1.949 Å)²⁵ and a saddled form (1.950 Å)²⁶ again emphasizing the importance of core conformation on the coordination group parameters. The average Cu–N_p distance in the dimer and trimer (10 unique distances) is 1.998 (4) Å. These are similar to values observed for planar [Cu(TPrP)] (2.000 Å)²⁷ and [Cu(OEP)] (1.998 Å).²⁸ The ruffled form of [Cu(TPP)] has shorter Cu–N_p bond distances as expected (1.981 Å).²⁹ The Pt–N_p bond distance in [Pt(porphine)] is 2.012 (7) Å. The effects of core conformation are less pronounced in other square-planar platinum porphyrins with 2.008 Å in ruffled [Pt(TPP)]³⁰ and the same distance in planar [Pt(OEP)].³¹ Two different platinum derivatives have Pt–N_p = 2.018 Å (planar, [Pt(TF₅PP)])³² and Pt–N_p = 2.008 (saddled, [Pt(TpNPh₂PP)]).³³

At one time no four-coordinate zinc porphyrins were known; the five-coordinate species with Zn–N_p distances of ~2.07 Å and out-of-plane displacements of 0.30 Å were thought to result from the large size of the zinc(II) ion that precluded four-coordinate species. Several four-coordinate zinc(II) species are now known, and the large size of the zinc is not quite so evident with Zn–N_p distances smaller than those of the five-coordinate species. Two distinct forms of [Zn(TPP)] have average Zn–N_p distances of 2.036 or 2.037 Å with the zinc precisely centered in the porphyrin plane.^{34, 35} The second derivative has quite asymmetric bond distances with Zn–N_p = 2.045 and 2.029 Å that were attributed to crystal packing effects.³⁵ Other derivatives include [Zn(OEP)] with Zn–N_p = 2.036 Å.³⁶ Two other derivatives have very sterically hindered cores: [Zn(TCHP)] has Zn–N_p = 2.029 Å with a stepped core.³⁷ [Zn(TPPBr₄)] has very asymmetric distances: 2.114 Å towards the brominated rings and 2.004 Å towards the nitrogen atoms of the unsubstituted rings.³⁸ The asymmetry results from a combination of steric and electronic effects.

Previous structural studies of some strongly overlapped four-coordinate derivatives where the porphyrin macrocycle was either OEP^{39, 40} or TMeP⁴¹ have suggested that the M–N_p bond most aligned with the overlapped pyrrole rings (and π – π interactions) could lead to asymmetry in the length of the M–N_p bonds. Observed differences were as large as 0.02 Å. In Table 2, we have tabulated the M–N_p bonds of the metalloporphyrins into two groups that would illuminate possible asymmetry. The data of the table provide no support for any asymmetry resulting from the π – π interactions of the porphyrin rings. We believe that observed asymmetries, if real, must originate in other effects such as crystal packing or asymmetric substitution on the ring periphery and not π – π interactions.

Prior studies^{14, 28, 36, 39, 40} had established that the [M(OEP)] series forms an isomorphous set of crystalline derivatives from Fe to Zn. These form linear 1-D chains with overlapped

and planar cores. The M–N_p bond distances follow the order Fe (1.996 Å) > Co (1.971 Å) > Ni (1.952 Å) < Cu (1.998 Å) < Zn (2.037 Å). The [M(TPP)] series^{29, 34, 35, 42, 43} also forms an isomorphous set of crystalline derivatives from Fe to Cu, the Zn derivatives are not part. This is likely because the series is a set of ruffled porphyrin cores, which is not likely for the zinc derivative with its large central ion. The M–N_p bond distance order follows the same order with Fe (1.972 Å) > Co (1.949 Å) > Ni (1.928 Å) < Cu (1.981 Å) < Zn (2.037 Å). The cobalt(II), copper(II) and one zinc(II) polymorph of the porphine derivatives are also isomorphous; the other form of zinc with its trimeric units is separate still. The M–N_p bond distance order for the porphines still follows the same order with Co (1.974 Å) > Ni (1.951 Å) < Cu (1.999 Å) < Zn (2.037 Å). The values for planar sets for OEP and porphine are nearly identical between element whereas the TPP set (except for Zn) has a bond distance difference of ~0.02 Å; the M–N_p bond distance in ruffled derivatives are always shorter.

Summary

A general method for the purification and preparation of crystals of the slightly soluble metalloporphines is given. The solid-state structures of the metalloporphines, the most sterically unhindered member of the porphyrin family, forms structures with inter-ring interactions. These include both dimeric and more unusually, trimeric structures. The trends in M–N_p bond distances follow along those found for the more commonly studies OEP and TPP derivatives.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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23. OEP, dianion of octaethylporphyrin; TPP, dianion of tetraphenylporphyrin; THCP, dianion of *meso*-cyclohexylporphyrin; TPPBr₄, dianion of 2,3,13,14-tetrabromotetraphenylporphyrin; TMeP, dianion of *meso*-tetramethylporphyrin; T(p-Me₂N)F₄PP, dianion of tetrakis(*o,o,m,m*-tetrafluoro-*p*-(dimethylamino)phenyl)porphyrin; T₅PP, dianion of tetrapentafluorophenylporphyrin; TpNPh₂PP, dianion of tetra(*p*-diphenylamino)phenylporphyrin; Ct, center of porphyrin ring; N_p, porphinato nitrogen atom; Py, pyridine.
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Figure 1. Diagram illustrating the geometric parameters used to describe the dimers (trimers) formed by two (three) porphine rings.

Figure 2.

ORTEP illustrations giving the side views of the dimer (top) and trimer (bottom) observed for [Co(porphine)]. 50% probability ellipsoids are shown. The atom labeling schemes are also illustrated.

Figure 3. ORTEP diagrams giving the top views of the dimer (top) and trimer (bottom) observed for [Co(porphine)]. 50% probability ellipsoids are shown.

Figure 4.

Mean plane diagrams for [Co(porphine)]. The top diagram is that for the central ring of the trimer, the second diagram is that for the outer rings of the trimer, and the bottom diagram is that for the ring of the dimer. Displacements of the atoms in each ring, in units of 0.01 Å, are given. Also displayed are the averaged values, for each ring, of all distinct groups of bond distances and bond angles.

Table 1

Brief Crystallographic Details for Four-Coordinate Metalloporphines

	[Zn(porphine)]#2	[Zn(porphine)]#1	[Pt(porphine)]	[Cu(porphine)]	[Co(porphine)]
chemical	C ₂₀ H ₁₂ N ₄ Zn	C ₂₀ H ₁₂ N ₄ Zn	C ₂₀ H ₁₂ N ₄ Pt	C ₂₀ H ₁₂ N ₄ Cu	C ₂₀ H ₁₂ N ₄ Co
FW	373.71	373.71	503.43	371.88	367.27
<i>a</i> , Å	10.0391(7)	10.0359(10)	10.1497(8)	10.0385(5)	10.0290(7)
<i>b</i> , Å	18.407(2)	12.5467(8)	11.9376(8)	12.5993(4)	12.5614(16)
<i>c</i> , Å	11.8122(9)	14.8377(7)	12.3200(8)	14.7750(11)	14.747(2)
<i>α</i> , deg	90	99.853(9)	90	99.691(14)	99.688(3)
<i>β</i> , deg	94.724(7)	93.007(4)	101.925(5)	92.907(4)	92.879(7)
<i>γ</i> , deg	90	97.742(5)	90	98.851(6)	98.748(9)
<i>V</i> , Å ³	2175.4(3)	1818.5(2)	1460.51(18)	1814.47(19)	1804.5(4)
space group	<i>P</i> ₂ /c	<i>P</i> $\bar{1}$	<i>P</i> ₂ /c	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>Z</i> , <i>Z'</i>	6, 1.5	5, 2.5	4, 1	5, 2.5	5, 2.5
temp, K	130	130	130	130	130
<i>D</i> _{calc} , g cm ⁻³	1.712	1.706	2.289	1.702	1.690
<i>μ</i> , mm ⁻¹	1.703	1.698	9.617	1.514	1.199
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0641 <i>wR</i> ₂ = 0.0817	<i>R</i> ₁ = 0.0387 <i>wR</i> ₂ = 0.0953	<i>R</i> ₁ = 0.0362 <i>wR</i> ₂ = 0.0848	<i>R</i> ₁ = 0.0713 <i>wR</i> ₂ = 0.1183	<i>R</i> ₁ = 0.0397 <i>wR</i> ₂ = 0.0955
final <i>R</i> indices (all data)	<i>R</i> ₁ = 0.0675 <i>wR</i> ₂ = 0.0892	<i>R</i> ₁ = 0.0519 <i>wR</i> ₂ = 0.1009	<i>R</i> ₁ = 0.0422 <i>wR</i> ₂ = 0.0875	<i>R</i> ₁ = 0.1056 <i>wR</i> ₂ = 0.1307	<i>R</i> ₁ = 0.0504 <i>wR</i> ₂ = 0.1007
<i>S</i>	1.054	1.099	1.193	1.083	1.026

Table 2
Summary of Geometric Features of Crystalline Four-Coordinate Metalloporphines

Compound	Form	M–N _p ^a	M···M ^a	Ct···Ct ^a	MPS ^a	L ₂ S ₂ ^a	ϕ^b
[Co(porphine)]	Dimer	1.972, 1.976	3.579	3.630	3.298	1.517	24.7
	Trimer	1.971, 1.975	3.611	3.642	3.260	1.626	26.5
[Cu(porphine)]	Dimer	1.994, 1.998	3.624	3.676	3.338	1.539	24.7
	Trimer	1.998, 2.002	3.651	3.681	3.288	1.656	26.7
[Zn(porphine)]#1	Dimer	2.032, 2.038	3.470	3.628	3.267	1.577	25.8
	Trimer	2.031, 2.041	3.563	3.660	3.240	1.700	27.7
[Zn(porphine)]#2	Trimer	2.038, 2.037	3.544	3.652	3.230	1.705	27.8
[Pt(porphine)]	Dimer	2.005, 2.018	3.759	3.749	3.369	1.643	26.0
[Ni(porphine)] ^c	Dimer	1.951, 1.951	3.716	3.716	3.355	1.597	25.4

^a Value in Å.

^b Value in degrees.

^c Data from reference 16.