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Crystal and Molecular Structure of (5,10,15,20-Tetra-*n*-propylporphinato)lead(II): A "Roof" Porphyrin

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The structure of (5,10,15,20-tetra-*n*-propylporphinato)lead(II) has been determined by three-dimensional X-ray diffraction. The compound crystallizes in space group $P\bar{1}$, with two molecules per unit cell and lattice constants $a = 11.732$ (3) Å, $b = 12.111$ (3) Å, $c = 11.114$ (2) Å, $\alpha = 112.56$ (1)°, $\beta = 91.85$ (2)°, and $\gamma = 72.85$ (2)°. The structure has been refined on F^2 by full-matrix least squares to $R_{F^2} = 0.057$ on the basis of 5570 reflections. Incorporation of the very large Pb(II) ion into the macrocyclic framework principally results in a *folding* distortion along an axis defined by two opposite methine carbons, rather than by a variation in distances and angles, when compared to free-base tetra-*n*-propylporphyrin. The molecules pack in pairs with a Pb–Pb distance of 4.256 Å, implying no direct metal–metal interaction. A pyrrole ring from a neighboring molecule lies 3.456 Å above the Pb(II) ion which suggests a weak π-axial linkage. The possibility that such a "roof" conformation plays a role in the trigger mechanism for the cooperative binding of oxygen by hemoglobin is considered.

Introduction

Lead(II) porphyrins exhibit unusual physical and chemical properties when compared to other metalloporphyrins. Theoretical considerations of their optical characteristics suggest that the Pb(II) ion should be considerably displaced from the nitrogen core of the porphyrin ring.[2] Pb(II) porphyrins also display anomalous "hyper" absorption spectra with split Soret bands attributed to charge transfer from the metal a_1 ($6p_z$) to the porphyrin e (π*) orbitals (for an assumed C_{4v} symmetry).[3] (Analogous transitions with the symmetry and oscillator strengths predicted for Pb hyperspectra have been observed in the hydroxylating heme enzyme, cytochrome P450.[4]) The redox chemistry of Pb porphyrins is also intriguing: oxidation of lead(II) octaethylporphyrin, PbOEP, leads to the expected π-cation radical PbOEP⁺·.[5,6] Abstraction of a second electron, however, yields[6] the dication Pb^{II}OEP^{2+} which undergoes internal conversion to [Pb^{IV}OEP]$^{2+}$.

To assess the influence of the large lead cation on the macrocyclic framework, we report here the first structural determination of a lead porphyrin (5,10,15,20-tetra-*n*-propylporphinato)lead(II) (PbTPrP). Because the structures of the homologous free-base[7] and Cu(II)[8] compounds are known, these results offer a sensitive test of changes in occupancy and increasing metal size on the conformation, angles, and bond distances of the porphyrin skeleton. Surprisingly, the macrocycle alleviates the strain imposed by the Pb ion by *folding* along an axis defined by two opposite methine carbons to yield a "roof" porphyrin. Such a conformation has, heretofore, not been observed for any fully conjugated porphyrin and may offer an alternative to the doming or puckering invoked as part of the trigger mechanism in the cooperative oxygenation of hemoglobin.[9–18]

Table I. Crystallographic Details[a]

Crystal Data	
formula: $C_{32}H_{36}N_4Pb$	$Z = 2$
fw: 683.2	$V = 1388$ Å³
space group: $P\bar{1}$	$\alpha = 112.56$ (1)°
$a = 11.732$ (3) Å[b]	$\beta = 91.85$ (2)°
$b = 12.111$ (3) Å	$\gamma = 72.85$ (2)°
$c = 11.114$ (2) Å	$\lambda = 1.540\,51$ Å for cell determination
ρ(calcd) = 1.63 g/cm³	

Data Collection Procedures

cryst form: block, {100}, {010}, {001}; $d(100) = 0.10$ mm, $d(010) = 0.06$ mm, $d(001) = 0.13$ mm

data collectn: CAD-4 diffractometer, using Ni-filtered Cu radiation, $\lambda = 1.542\,42$ Å

T: 20 °C

linear abs coeff: $\mu = 119.7$ cm⁻¹ (analytical absorption corrections calculated by the program ABSOR[22])

data range: $0 \leqslant 2\theta \leqslant 154°, h \geqslant 0$

no. of reflections: 11 913

unique reflections: 5570

agreement on merging: 0.03 (4154 multiple determinations)

scattering factors: Cromer and Mann;[23a] Stewart, Davidson, and Simpson[23b]

anomalous dispersion: Cromer and Liberman[23c]

refinement: full-matrix least squares on F^2 in two blocks

$R_{F^2} = 0.059$, where $R_{F^2} = \Sigma |F_o{}^2 - F_c{}^2|/\Sigma |F_o{}^2|$

$R_{wF^2} = 0.075$, where $R_{wF^2} = [\Sigma(w(F_o{}^2 - F_c{}^2))^2/\Sigma(wF_o{}^2)^2]^{1/2}$

$S = 1.44$, where $S = [\Sigma(w(F_o{}^2 - F_c{}^2))^2/(N_o - N_v)]^{1/2}$ [c]

$w = 1/\sigma_{F_o{}^2}{}^2$ and $\sigma_{F^2}{}^2 = \sigma^2 + (0.020I)^2$

[a] Programs used are described in the CRYSNET manual of Brookhaven National Laboratory.[22] [b] The figures in parentheses are the standard deviation of the least significant digit here and throughout this paper. [c] The quantities $F_o{}^2$ and $F_c{}^2$ are the observed and calculated squared structure factor amplitudes, w is the experimental weight, and N_o and N_v are the number of observations and variables, respectively.

Experimental Section

meso-Tetra-*n*-propylporphyrin was synthesized by reaction of pyrrole with *n*-butyraldehyde in xylene containing 0.1 M trifluoroacetic acid[19] and purified by chromatography on dry alumina with chlo-

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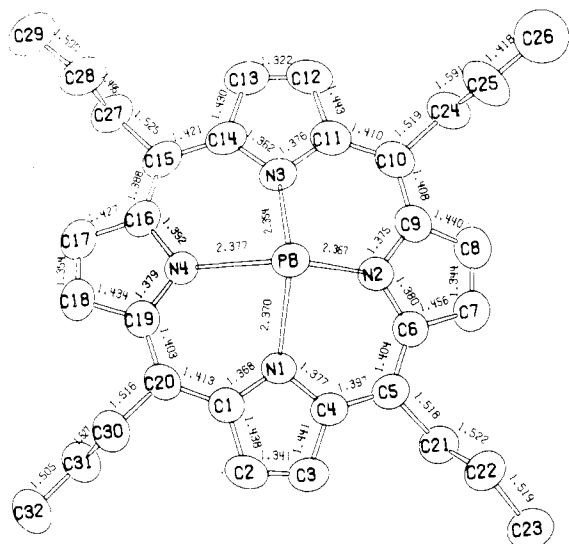
Figure 1. Structure of (5,10,15,20-tetra-*n*-propylporphinato)lead(II), atom numbering scheme, and bond distances. Hydrogen atoms have been omitted. The thermal ellipsoids have been drawn for 50% probability. The standard deviation on a typical C–C bond length is 0.005, and the standard deviation on a Pb–N bond length is 0.004.

roform. The purified porphyrin was reacted with lead acetate in refluxing *N,N'*-dimethylformamide, and the product was precipitated with water and recrystallized from heptane. PbTPrP exhibited the expected "hyper" spectrum[3] in benzene: λ_{max} = 355, 450 (sh), 470, 520, 575, and 675 nm. The features were parallel to those of lead(II) *meso*-tetraphenylporphyrin[20] but red shifted. Anal. Calcd for $PbC_{32}H_{36}N_4$: C, 56.24; H, 5.31; N, 8.19. Found:[21] C, 56.12; H, 5.52; N, 8.10.

Although the irregularly shaped crystals showed morphological evidence of twinning, a few dark green, almost black single crystals were extracted from the sample. Preliminary precession photography indicated only a triclinic cell. A computerized examination of the Niggli matrix of the Buerger-reduced cell did not indicate a lattice of higher symmetry.[24] The cell constants and their standard deviations were determined on a CAD-4 diffractometer. Experimental details are given in Table I. During the month of data collection, the intensities of three reflections were monitored after each 100 reflections to check for experimental stability. Analysis of these standards showed no fluctuations beyond those expected on the basis of counting statistics.

Solution and Refinement of Structure

The Pb atom was located from a Patterson map. Standard difference Fourier and least-squares techniques were used to complete the structural model. Stereochemically sensible maxima for all hydrogen atoms were present in a difference map, but these atoms were placed in calculated positions, with C–H distances of 1.00 Å, standard bond angles and torsion angles, and isotropic thermal parameters *B* of 6.0 Å². These positions were periodically updated. The positional and anisotropic thermal parameters for all nonhydrogen atoms were varied until the refinement converged. A final difference Fourier map
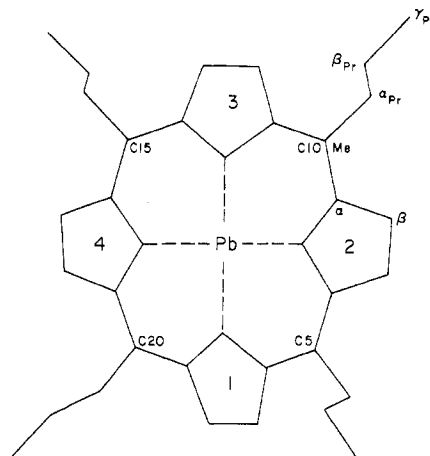
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Figure 2. Structural formula and atom designations for PbTPrP.
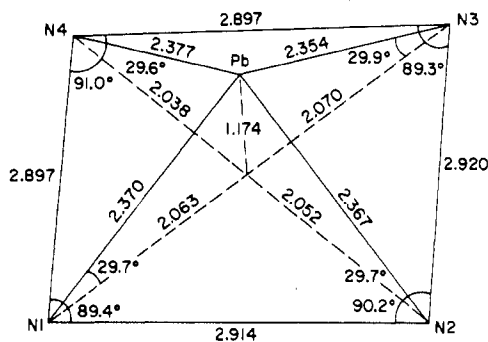

Figure 3. Coordination geometry of the lead ion.

was featureless, except for a peak of density 1.00 e/Å³ located 1.95 Å from N(1) and 2.22 Å from N(4). This peak was also 2.33 Å from Pb, below the plane of the ring. The final positional and thermal parameters for nonhydrogen atoms are given in Table II. Coordinates for the hydrogen atoms have been deposited, as has a tabulation of the observed and calculated squared structure factors. Ordering information is given on any current masthead page.

Results

The molecular structure of PbTPrP is shown in Figure 1, which displays the atomic numbering scheme and bond distances. Atom designation and ring numbering are sketched in Figure 2. Selected bond angles are presented in Table III.

As judged by the bond distances for the macrocycle, which are similar to those found in H_2TPrP[7] and CuTPrP,[8] incorporation of the large Pb(II) ion into the porphyrin skeleton does not significantly alter any nearest-neighbor bond distances. With one exception, the second neighbors are also unaffected as measured by the bond angles in H_2TPrP, CuTPrP, and PbTPrP. In CuTPrP, the average C_α–C_{Me}–C_α angle is diminished by 2.2° from the value of 125.0° in H_2TPrP, indicating a contraction of the pyrroles toward the Cu(II) ion, with maintenance of the C_{Me}–C_α bond distances.[7,8] The average internal angle about C_{Me} in the present study is 125.1°, i.e., near the free-base value.

Comparison of the sizes of the central cores of the three complexes is also useful. This effective size may be expressed in the distances between opposite N atoms of 4.133 (6) Å and 4.090 (6) Å as given in Figure 3. The analogous distances of N(1) to N(3) and N(2) to N(4) in H_2TPrP are 4.160 and 4.080 Å,[7] while those in CuTPrP are 4.010 and 3.988 Å.[8] The angle of 125.1° about C_{Me} coupled with the similarity in core size between H_2TPrP and PbTPrP seem to indicate that the TPrP ligand in the latter structure does not expand to accommodate the Pb. As in CuTPrP,[8] the crystallographic analysis provides no evidence for coordination of solvent molecules in the axial positions.

Table II. Final Positional and Thermal Parameters^a for the Nonhydrogen Atoms of PbTPrP ($\times 10^4$)

ATOM	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{33}
PB	-229.1(17)	5706.8(19)	7078.5(21)	463(1)	512(1)	590(1)	-90(1)	-50(1)	310(1)
N1	-1439(3)	4807(4)	7841(4)	470(22)	518(22)	538(24)	-152(18)	-34(18)	243(19)
N2	-55(3)	6427(4)	9359(4)	506(22)	509(22)	525(24)	-147(18)	-68(19)	249(19)
N3	1854(3)	5189(4)	7225(4)	417(21)	569(23)	671(28)	-91(18)	-20(19)	300(21)
N4	508(3)	3518(3)	578(4)	482(23)	473(22)	542(26)	-110(18)	-21(19)	211(19)
C1	-1962(4)	3992(5)	6972(5)	521(28)	528(27)	597(32)	-147(22)	-86(24)	251(24)
C2	-3056(5)	4094(6)	7612(6)	554(32)	703(35)	899(45)	-278(28)	-98(30)	351(33)
C3	-3167(5)	4927(6)	8851(6)	581(32)	678(34)	784(41)	-199(27)	56(29)	303(31)
C4	-2149(4)	5391(5)	9009(5)	513(27)	523(26)	614(32)	-131(22)	-1(24)	281(25)
C5	-1923(4)	6272(5)	10164(5)	580(30)	531(26)	574(31)	-99(23)	14(24)	311(24)
C6	-922(4)	6709(4)	10332(5)	560(29)	483(25)	555(30)	-121(22)	-72(23)	265(23)
C7	-653(5)	7574(5)	11555(5)	736(37)	627(33)	512(32)	-167(29)	-79(27)	207(26)
C8	345(5)	7797(5)	11282(6)	765(39)	619(33)	667(38)	-215(30)	-132(31)	197(29)
C9	740(5)	7075(5)	9916(5)	607(31)	517(27)	673(35)	-174(24)	-105(27)	249(26)
C10	1794(5)	7006(5)	9283(6)	607(32)	627(32)	761(40)	-248(27)	-157(29)	292(30)
C11	2339(5)	6073(5)	8058(6)	518(29)	586(30)	843(41)	-159(24)	-84(28)	354(30)
C12	3549(5)	5808(6)	7548(7)	595(35)	864(44)	1079(55)	-345(33)	-141(35)	445(41)
C13	3765(5)	4783(6)	6464(7)	522(32)	863(43)	953(49)	-216(31)	3(32)	417(38)
C14	2721(4)	4376(5)	6242(6)	451(26)	668(32)	728(37)	-85(24)	-6(25)	399(29)
C15	2621(4)	3267(5)	5222(5)	487(27)	645(31)	612(33)	12(23)	6(24)	363(27)
C16	1609(4)	2871(5)	5040(5)	568(29)	538(27)	555(31)	-34(23)	19(24)	297(24)
C17	1510(5)	1750(5)	4027(6)	748(38)	522(30)	686(37)	-45(27)	79(30)	254(27)
C18	365(5)	1740(5)	4115(6)	869(42)	528(30)	602(35)	-151(29)	14(31)	188(26)
C19	-266(5)	2838(5)	5223(5)	608(30)	540(27)	540(30)	-157(24)	-77(24)	251(24)
C20	-1450(5)	3112(5)	5709(5)	605(31)	570(28)	601(33)	-240(25)	-161(26)	277(25)
C21	-2839(5)	6795(5)	11334(5)	718(35)	647(32)	586(33)	-184(27)	21(27)	319(27)
C22	-3898(5)	7904(5)	11379(6)	659(35)	648(34)	700(38)	-97(28)	93(29)	274(30)
C23	-4832(6)	8338(7)	12513(7)	821(45)	857(46)	944(51)	-228(37)	198(38)	286(40)
C24	2395(6)	8002(6)	9988(7)	773(42)	798(43)	970(51)	-427(36)	-102(37)	272(38)
C25	1881(7)	9174(7)	9590(10)	994(58)	733(46)	1810(90)	-519(45)	-33(57)	167(53)
C26	2372(9)	10166(9)	10233(10)	1576(91)	1070(69)	1500(89)	-422(66)	180(70)	458(64)
C27	3713(5)	2433(6)	4246(6)	565(32)	737(36)	762(40)	5(27)	50(28)	419(32)
C28	3731(5)	2669(6)	3022(7)	626(36)	897(44)	880(47)	-59(32)	77(32)	494(38)
C29	4797(6)	1785(7)	2074(7)	840(47)	1102(56)	846(49)	-119(41)	123(38)	502(44)
C30	-2191(5)	2310(5)	4888(6)	689(35)	625(32)	633(36)	-196(28)	-159(28)	245(28)
C31	-2053(5)	1111(6)	5112(6)	746(38)	672(35)	750(41)	-258(30)	-183(34)	296(31)
C32	-2928(6)	364(6)	4299(7)	988(45)	670(37)	877(47)	-312(34)	-217(37)	242(34)

a The form of the anisotropic vibration factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table III. Selected Angles (Deg) around Nonhydrogen Atoms

N-Pb-N (Adjacent)

N(1)-Pb-N(2)	75.9 (1)	N(2)-Pb-N(3)	76.4 (1)
N(1)-Pb-N(4)	75.2 (1)	N(3)-Pb-N(4)	75.5 (1)

N-Pb-N (Opposite)

N(1)-Pb-N(3)	122.0 (1)	N(2)-Pb-N(4)	119.0 (1)

C_α-N-C_α

C(1)-N(1)-C(4)	107.7 (4)	C(11)-N(3)-C(14)	106.9 (4)
C(6)-N(2)-C(9)	107.5 (4)	C(16)-N(4)-C(19)	107.1 (4)

C_α-C_{Me}-C_α

C(4)-C(5)-C(16)	125.6 (5)	C(14)-C(15)-C(16)	125.4 (5)
C(9)-C(10)-C(11)	124.9 (5)	C(1)-C(20)-C(19)	124.6 (5)

N-C_α-C_β

N(1)-C(4)-C(3)	108.5 (5)	N(3)-C(11)-C(12)	109.0 (5)
N(1)-C(1)-C(2)	108.3 (5)	N(3)-C(14)-C(13)	108.5 (5)
N(2)-C(6)-C(7)	108.8 (4)	N(4)-C(16)-C(17)	108.5 (5)
N(2)-C(9)-C(8)	108.5 (5)	N(4)-C(19)-C(18)	108.8 (5)

N-C_α-C_{Me}

N(1)-C(1)-C(20)	125.5 (5)	N(2)-C(11)-C(10)	125.6 (5)
N(1)-C(4)-C(5)	126.2 (5)	N(3)-C(14)-C(15)	125.2 (5)
N(2)-C(6)-C(5)	125.7 (5)	N(4)-C(16)-C(15)	125.9 (5)
N(2)-C(9)-C(10)	126.2 (5)	N(4)-C(19)-C(20)	126.0 (5)

C_α-C_β-C_β

C(1)-C(2)-C(3)	108.2 (5)	C(11)-C(12)-C(13)	106.4 (5)
C(4)-C(3)-C(2)	107.2 (5)	C(14)-C(13)-C(12)	109.2 (5)
C(6)-C(7)-C(8)	106.6 (5)	C(16)-C(17)-C(18)	108.0 (5)
C(9)-C(8)-C(7)	108.7 (5)	C(19)-C(18)-C(17)	107.6 (5)

C_β-C_α-C_{Me}

C(3)-C(4)-C(5)	125.3 (5)	C(13)-C(14)-C(15)	126.2 (5)
C(7)-C(6)-C(5)	125.3 (5)	C(17)-C(16)-C(15)	125.6 (5)
C(8)-C(9)-C(10)	125.3 (5)	C(18)-C(19)-C(20)	125.0 (5)
C(12)-C(11)-C(10)	125.1 (5)	C(2)-C(1)-C(20)	125.9 (5)

The Pb-N bond lengths are somewhat irregular with three of the four Pb-N distances within 0.006 Å of 2.371 Å, while the fourth is 2.354 (4) Å. The geometry about the lead ion is illustrated in Figure 3. While no explanation for the diminution of the Pb-N(3) bond is evident, it is worth noting that Pb(II)-N distances vary widely, with published values ranging from 2.21 Å in lead(II) phthalocyanine[25] to 2.99 Å in bis(10-methylisoalloxazine)lead(II) perchlorate tetrahydrate.[26]

The Pb(II) ion is located 1.174 Å from the least-squares plane through the four nitrogen atoms. This large displacement was expected due to the large size of the metal and indicates the strain upon the macrocycle in attempting to accommodate the Pb(II). The ligand is not planar, although the individual pyrrole rings are flat to within 0.015 Å. Each of the four seven-atom fragments that comprise a pyrrole ring and its attached methine carbon atoms are also planar to within 0.08 Å.

As a whole, the ligand is best described as being folded along the imaginary line between C(10) and C(20) and differs substantially from the C_{4v} domed geometry predicted for Pb(II) porphyrins.[27] The ligand half consisting of rings 1 and 2 and C(5) and that comprising rings 3 and 4 and C(15) define two planes which are inclined 22° to one another. The two rings of each half are coplanar to within 5.0°. This folding is not known for any other fully conjugated tetrapyrrole metallomacrocycle but has been observed in (5,20-dimethyl-5,20-dihydrooctaethylporphinato)oxotitanium(IV)[28] and -nickel(II)[29] complexes. In addition to the dominant distortion, the two ligand halves are slightly twisted, with respect to one another, as indicated by the displacements of C(10) and C(20) in planes 11 and 12 shown in Table IV.

The conformational asymmetry of the molecule is further exemplified by the orientations of the side chains. Three of the four propyl groups are directed toward the same side of the plane of the macrocycle as the metal, whereas the fourth

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Table IV. Displacements (Å) from Some Mean Planes[a]

1. $2.593x - 9.394y + 8.043z - 1.447 = d$

N(1)	-0.029^c	N(4)	0.029
N(2)	0.029	Pb[b]	-1.174
N(3)	-0.029		

2. $2.494x - 9.458y + 8.042z - 1.525 = d$

C(15)	0.239	C(20)	-0.239
C(10)	-0.238	Pb[b]	-1.287
C(5)	0.238		

3. $3.293x - 9.581y + 6.855z - 0.3008 = d$

N(1)	-0.005	C(3)	0.004
C(1)	0.008	C(4)	0.003
C(2)	-0.010		

4. $3.666x - 9.609y + 6.049z + 5.338 = d$

N(2)	-0.001	C(8)	-0.008
C(6)	-0.001	C(9)	0.005
C(7)	0.006		

5. $1.638x - 9.215y + 8.969z - 2.007 = d$

N(3)	-0.005	C(13)	0.002
C(11)	0.008	C(14)	0.005
C(12)	-0.007		

6. $1.029x - 8.928y + 9.527z + 2.414 = d$

N(4)	0.004	C(18)	-0.001
C(16)	-0.010	C(19)	0.000
C(17)	0.015		

7. $3.045x - 9.6381y + 7.0928z - 0.5435 = d$

N(1)	-0.053	C(4)	-0.004
C(1)	-0.044	C(5)	0.035
C(2)	-0.021	C(20)	0.065
C(3)	0.021		

8. $3.454x - 9.723y + 6.146z + 0.5083 = d$

N(2)	-0.008	C(9)	-0.021
C(6)	0.016	C(5)	-0.007
C(7)	0.020	C(10)	0.021
C(8)	-0.021		

9. $2.024x - 9.114y + 8.838z - 2.105 = d$

N(3)	-0.073	C(14)	-0.026
C(11)	-0.044	C(15)	0.064
C(12)	-0.009	C(10)	0.077
C(13)	0.011		

10. $1.365x - 8.807y + 9.481z - 2.449 = d$

N(4)	0.002	C(19)	-0.033
C(16)	0.020	C(20)	0.025
C(17)	0.034	C(15)	-0.018
C(18)	-0.030		

11. $3.486x - 9.582y + 6.513z + 0.0264 = d$

N(1)	0.026	C(6)	0.006
N(2)	-0.055	C(7)	0.068
C(1)	0.059	C(8)	0.024
C(2)	-0.003	C(9)	-0.036
C(3)	-0.034	C(10)[b]	-0.015
C(4)	-0.020	C(20)[b]	0.257
C(5)	-0.033		

12. $1.459x - 8.971y + 9.298z - 2.320 = d$

N(3)	0.019	C(16)	0.026
N(4)	-0.027	C(17)	0.075
C(11)	0.066	C(18)	-0.001
C(12)	0.006	C(19)	-0.049
C(13)	-0.051	C(10)[b]	0.288
C(14)	-0.045	C(20)[b]	-0.015
C(15)	-0.013		

13.[d] $8.203x - 9.534y + 7.770z - 1.5729 = d$

N(1)	-0.179	N(3)	-0.197
C(1)	0.239	C(11)	-0.242
C(2)	-0.099	C(12)	-0.092
C(3)	0.081	C(13)	0.063
C(4)	0.027	C(14)	0.004
C(5)	0.178	C(15)	0.210
N(2)	-0.140	N(4)	-0.118
C(6)	0.154	C(16)	0.181
C(7)	0.394	C(17)	0.405
C(8)	0.212	C(18)	0.192
C(9)	-0.104	C(19)	0.120
C(10)	-0.280	C(20)	-0.291
		Pb[b]	-1.702

[a] The displacement (d) for any atom may be calculated by using the fractional coordinates in the indicated equation. [b] This atom was not included in the calculation of the mean plane. [c] The average esd on d is 0.005 Å. [d] Included for reference purposes only.

Table V. Intramolecular Distances Less Than 2.5 Å between Hydrogen Atoms

H(2)–H(301)	2.216	H(12)–H(242)	2.073
H(3)–H(211)	2.132	H(13)–H(271)	2.104
H(7)–H(212)	2.054	H(17)–H(272)	2.103
H(8)–H(241)	2.035	H(18)–H(302)	2.246

(on C(20)) is directed away from the Pb(II).

The PbTPrP molecules pack in pairs as shown in Figure 4. The distance between adjacent Pb(II) ions of 4.256 Å is somewhat longer than a Pb–Pb contact[30] and implies no direct metal–metal interaction. However, pyrrole ring 4 of the neighboring molecule lies 3.465 Å above the Pb(II) ion. Since the half-thickness of an aryl system is 1.7 Å, this contact suggests that the adjacent ring forms a weak π-axial linkage. In the crystal, there are no intermolecular C–C or C–N distances less than 3.3 Å, although within the molecule, the eight hydrogen atoms of the pyrrole rings are 2.0 Å away from the hydrogen atoms on the α-carbons of the propyl groups (Table V). These contacts hinder free rotation of the propyl groups and, because of the asymmetric conformation of the macrocycle, render the two hydrogen atoms inequivalent. Electron spin resonance results on cation radicals of tetrapropyl- and other tetraalkylporphyrins indeed indicate that the methylene groups display restricted rotation.[19,31]
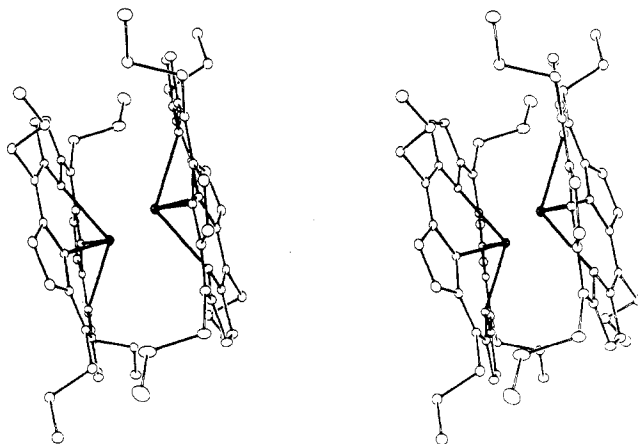

Figure 4. A stereoscopic view of the interaction between two PbTPrP molecules.

The unusual roof conformation of the PbTPrP suggests an intriguing possibility. The various mechanisms proposed to rationalize the cooperativity observed in hemoglobin upon oxygen binding include a porphyrin rearrangement in which the macrocycle is originally puckered or domed and converts

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to a more planar conformation on oxygenation thereby triggering a protein conformational change.[9–18] Although the iron displacement in deoxy hemoglobin is clearly not as extreme as that of Pb in PbTPrP, a *folding* of the porphyrin along the C_α–C_γ axis, because of constraints imposed peripherally by the protein and axially via the proximal histidine, has not been previously considered for deoxy hemoglobin. The results presented here indicate that such bending has no major effect on bond distances and angles[32] and suggest that a "roof" structure may be an alternate possibility. Existing X-ray results on deoxy hemoglobin and myoglobin do not exclude such a conformation.[33,34] Furthermore, analysis[35] of the at-

omic coordinates[36] obtained from the 1.4-Å resolution study of erythrocruorin, the monomeric hemoglobin found in the insect *Chironomus thummi thummi*, clearly indicates that a dominant distortion of its deoxy form is indeed a folding of the macrocycle along its C_α–C_γ axis with an angle of 7.2°.

Registry No. PbTPrP, 73395-80-9.

Supplementary Material Available: A table of fractional coordinates for the hydrogen atoms and a listing of observed and calculated squared structure factors (33 pages). Ordering information is on any current masthead page.

(32) As noted above, incorporation of the Pb has no major effect on these parameters when compared to H₂TPrP. The core is expanded relative to CuTPrP.
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Molecular and Crystal Structure of a Metalloporphyrin Containing the MoO₂²⁺ Unit: *cis*-Dioxo(5,10,15,20-tetra-*p*-tolylporphyrinato)molybdenum(VI), MoO₂(TTP)

BERNARD F. MENTZEN,* MICHEL C. BONNET, and HENRY J. LEDON

The molecular structure of MoO₂(TTP), where TTP is the dianion of 5,10,15,20-tetra-*p*-tolylporphyrin, has been determined from X-ray single-crystal analysis. The complex crystallizes in the triclinic $P\bar{1}$ space group with a = 11.554 (3) Å, b = 13.128 (5) Å, c = 16.794 (4) Å, α = 108.04 (2)°, β = 92.09 (2)°, γ = 108.37 (3)°, and Z = 2 formula units per unit cell. The structure was solved by the heavy-atom method, and full-matrix least-squares refinement has led to a final value of R (R_w) index of 0.0690 (0.0677) based on 2112 unique reflections. The molybdenum atom is hexacoordinated in a distorted trigonal prism by the four pyrrole nitrogen atoms and the two oxygen atoms. The Mo–O bond lengths in the cis MoO₂ moiety are 1.709 (9) and 1.744 (9) Å. Two sets of Mo–N distances are observed: Mo–N₁ = 2.245 (9), Mo–N₃ = 2.247 (9) Å; Mo–N₂ = 2.165 (6), Mo–N₄ = 2.149 (7) Å. The molybdenum atom lies 1.095 (9) Å out of the mean plane formed by the 20 carbon atoms of the core (C-20). The porphyrin core shows a strong "horse saddle"-type deformation.

In the past few years, synthesis, structural characterization, and reactivity of molybdenum porphyrins have received considerable attention.[1–7] We recently described the photolysis

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Table I. Summary of Crystal Data and Intensity Collection

MoO₂(TTP)·³/₂C₇H₈	
mol wt	935.0
space group	$P\bar{1}$
a, Å	11.554 (3)
b, Å	13.128 (5)
c, Å	16.794 (4)
α, deg	108.04 (2)
β, deg	92.09 (2)
γ, deg	108.37 (3)
V, Å³	2273.0
cell content	2 (C₄₈H₃₆N₄O₂Mo·³/₂C₇H₈)
ρ(calcd), g cm⁻³	1.37
ρ(obsd, flotation), g cm⁻³	1.4
cryst dimens, mm	0.3 × 0.3 × 0.2
μ, cm⁻¹	3.27
scan speed, deg min⁻¹	10.06–2.51 (most at 2.87)
measd reflctns	6855
obsd reflctns used	2112, $I > 2\sigma(I)$
refined scale factor	0.1548 (62)

of a diperoxomolybdenum(VI) porphyrin Mo(O₂)₂(TTP), affording a complex of molecular formula MoO₂(TTP) for which we proposed a *cis*-dioxomolybdenum(VI) structure.[2c] To the best of our knowledge, if compounds containing the