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Trioxygen-Bridged Porphyrin Dimers with Unusual Molecular Geometries. X-Ray Crystal Structures of $\{(\mu\text{-OH})_3[Zr(OEP)]_2\}(7,8\text{-}C_2B_9H_{12})$ and $(\mu\text{-O})(\mu\text{-OH})_2[Zr(TPP)]_2$

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The X-ray structures of the title complexes revealed that the two zirconium porphyrin moieties are joined either by three bridging hydroxo ligands or by one oxo and two hydroxo ligands. In both structures, the two porphyrin macrocycles are perfectly or nearly eclipsed and concomitantly one of the Zr-O bonds eclipses one of the Zr-N bonds. Such unprecedented eclipsed conformation found in both structures strongly suggests that it is stabilized by d_π-p_π interactions between Zr and O and N atoms despite the unfavorable steric interactions.

Although two metalloporphyrins linked at the metal through a single atom, such as μ-oxo-porphyrin dimers are well known, two or more atom-bridged porphyrin dimers are rare.1) Perhaps $O_3Nb_2(TPP)_2$ (TPP = 1,5,10,15-tetraphenylporphyrin dianion)2,3) is the only triatom-bridged dimer whose structure was confirmed by X-ray crystallography. Here we report two novel trioxygen-bridged porphyrin dimers in which *two porphyrin macrocycles are eclipsed*: the formation, characterization and X-ray structures of $\{(\mu\text{-OH})_3[Zr(OEP)]_2\}(7,8\text{-}C_2B_9H_{12})$ (OEP = octaethylporphyrin dianion) and $(\mu\text{-O})(\mu\text{-OH})_2[Zr(TPP)]_2$.

In an attempt to synthesize $Zr(OEP)(\eta^5\text{-}C_2B_9H_{11})$4,5) by the reaction of $Zr(OEP)Cl_2$5,6) with $Tl_2(C_2B_9H_{11})$,7) we adventitiously obtained $\{(\mu\text{-OH})_3[Zr(OEP)]_2\}(7,8\text{-}C_2B_9H_{12})$ (**1**)8) instead which was presumably formed by the hydrolysis of either $Zr(OEP)Cl_2$ or $Zr(OEP)(\eta^5\text{-}C_2B_9H_{11})$. The compound has been characterized by various spectroscopic methods8) and by X-ray crystallography.9)

The structure of the cation in **1** is shown in Fig. 1. The two zirconium(IV) porphyrin moieties are joined together by three bridging hydroxo ligands. The cation lies on a mirror plane containing the two Zr atoms, O1, N2 and N3 (also O1', N2' and N3')10) atoms. In addition, a twofold axis perpendicular to the mirror plane passes through O2 (also O2",10)see Fig. 2) which requires the upper and lower halves of the dimer to be structurally equivalent and also the two porphyrin planes to be exactly parallel. However, the plane and twofold symmetries lead to the disorder of the bridging oxygen atoms; the three bridging oxygen atoms take one of the four equally-probable orientations, two of which (**A** and **B**) are illustrated in Fig. 2 (the other two are related to these two by the inversion symmetry).

Despite some variations in bond distances the oxygen atoms form rather symmetric bridges between the two Zr atoms: the Zr-O bond distances range from 2.078(15) to 2.227(12) Å with the average value of 2.152(49) Å; the Zr-O-Zr angles are in the range 97.8(8) - 100.1(6)° (average, 98.2(14)°). These bond parameters are not exceptional.11) The distance between the two metal centers in **1** (3.252(1) Å) is much longer than that in $O_3Nb_2(TPP)_2$ (2.872(1)[2] or 2.751(4)[3]) reflecting the fact that metal-hydroxo bonds are longer than metal-oxo bonds. As in $O_3Nb_2(TPP)_2$ [2,3] the coordination polyhedron around each metal is of a 4+3 type with the square-planar base provided by the porphyrin nitrogen atoms and the trigonal-planar cap provided by the hydroxo oxygen atoms. The planes defined by the base and the cap are nearly parallel (dihedral angles: 1(4)° in **A** and 3(4)° in **B**). All the Zr-N distances are equal with the average value of 2.223(5) Å and the Zr atom is displaced 0.942 Å out of the N_4 plane.

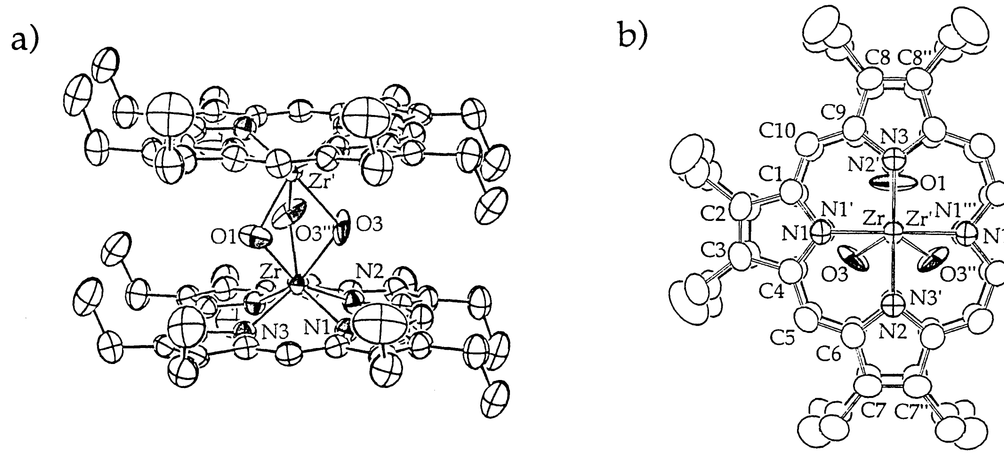

Fig. 1. Structure of the cation in **1**.[10] a) side view, b) top view. Only one orientaion (**A**, see text and Fig. 2) for the three disordered oxygen atoms is shown. Selected distances [Å] and angles [°]: Zr-O1 2.115(20), Zr'-O1 2.202(22), Zr-O3 2.078(15), Zr'-O3 2.165(15), Zr-N1 2.223(4), Zr-N2 2.214(5), Zr-N3 2.232(6), Zr-O1-Zr' 97.8(8), Zr-O3-Zr' 100.1(6), O1-Zr-O3 71.4(6), O1-Zr'-O3 68.2(5), O3-Zr-O3" 66.4(5), O3-Zr'-O3" 63.4(5), O1-Zr-N3 73.9(6), O1-Zr-N2' 74.3(5).

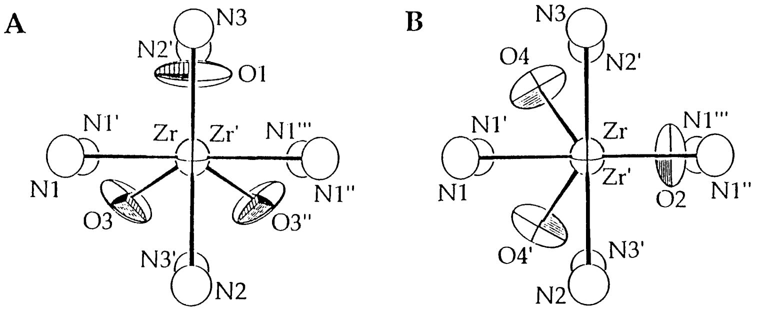

Fig. 2. Two (**A** and **B**) of the four equally-probable orientations for the three disordered oxygen atoms in **1**.[10] The other two are related these two by the inversion symmetry. Selected distances [Å] and angles [°] for the orientation **B**: Zr-O2 2.158(11), Zr-O4 2.122(11), Zr-O4' 2.227(12), Zr-O1-Zr' 97.8(8), Zr-O4-Zr' 96.8(5), O2-Zr-O4 72.9(5), O2-Zr-O4' 70.9(4), O4-Zr-O4' 65.7(4), O2-Zr-N1" 74.3(5).

The most striking feature of the structure is that *the two porphyrin rings are almost perfectly eclipsed* (Fig. 1b): the torsion angles N3-Zr-Zr'-N2' and N1-Zr-Zr'-N1' are 0° (crystallographically required) and 0.7°, respectively. Such ecliped conformation of the porphyrin dimer is unprecedented.[12] The eclipsed conformation also distinguishes the present structure from the two known structures of $O_3Nb_2(TPP)_2$; the two porphyrin rings in the latter are either slipped[2] or staggered.[3] It is also interesting to note that one of the Zr-O bonds (Zr-O1 in **A** or Zr-O2 in **B**) eclipses a Zr-N bond (Fig. 2).

We also obtained another trioxygen-bridged dimer (μ-O)(μ-OH)$_2$[Zr(TPP)]$_2$ (**2**)[13] accidentally in an attempt to grow crystals of Zr(TPP)Me_2[5] presumably as a result of the hydrolysis of the dimethyl complex. The dimer has been fully characterized by spectroscopy[13] and X-ray crystallography.[9]

The core structure of **2** is similar to that of **1**, but in **2** the two Zr(IV) atoms are linked by one oxo and two hydroxo ligands (Fig. 3). The molecule lies on a twofold axis passing through the bridging oxo ligand and the midpoint between the two Zr atoms. In the structure of **2** the oxo and hydroxo ligands were clearly distinguished: the Zr-O(oxo) distance (1.981(5) Å) is shorter than the Zr-O(hydroxo) distances (2.176(6) and 2.181(6) Å); the Zr-O-Zr angle for the oxo (101.7(4)°) is larger than that for the hydroxo (89.7(2)°). The larger Zr-O-Zr angle for the oxo bridge makes the two porphyrin planes no longer parallel (dihedral angle, 12.7°). The presence of the bridging oxo ligand also leads to the considerably shorter Zr···Zr distance (3.071(1) Å) compared to that in **1** (3.252(1) Å). The average Zr-N distance amounts to 2.290(22) Å and the displacement of the metal from the N_4 plane is 1.057 Å.

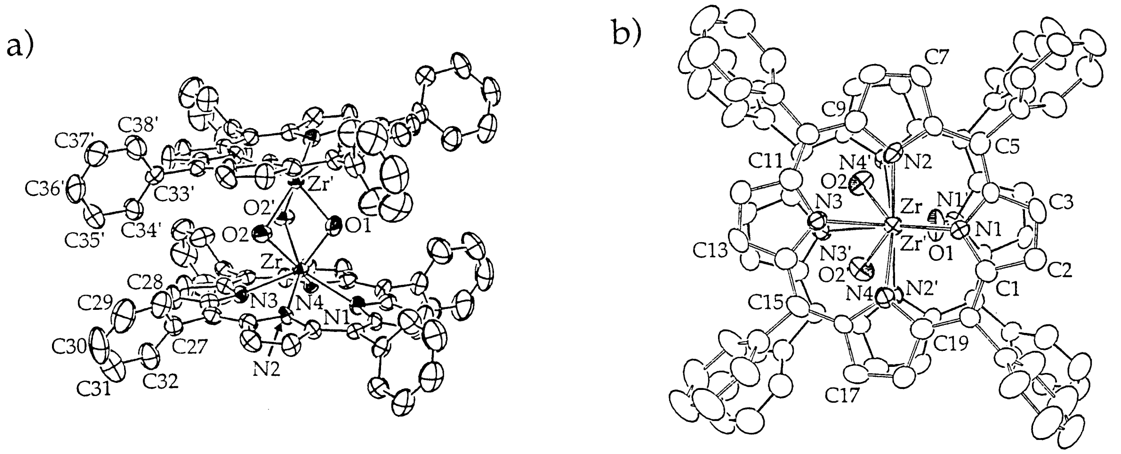

Fig. 3. Structure of **2**. a) side view, b) top view. Selected distances [Å] and angles [°]: Zr-O1 1.981(5), Zr-O2 2.176(6), Zr-O2' 2.181(6), Zr-N1 2.266(6), Zr-N2 2.294(5), Zr-N3 2.324(6), Zr-N4 2.274(6) Zr-O1-Zr' 101.7(4), Zr-O2-Zr' 89.7(2), O1-Zr-O2 73.7(2), O1-Zr-O2' 73.6(2), O2-Zr-O2' 69.8(2), O1-Zr-N1 84.3(2), O2-Zr-N2 79.9(2), O2-Zr-N3 80.6(2), O2'-Zr-N3 84.9(2), O2'-Zr-N4 76.5(2).

Most importantly, here also *the two porphyrin rings are almost eclipsed* (Fig. 3b): the N1-Zr-Zr'-N1' torsion angle is 7.8°. The near ecliped conformation of the porphyrin cores leads to the close contacts of the peripheral phenyl groups on the two opposite porphyrin rings (Fig. 3); the shortest intramolecular C···C distance (C28···C34') is 3.409(13) Å. As in **1** one of the Zr-O bonds (Zr-O1(oxo)) eclipses a Zr-N bond (Zr-N1) (twist angle, 3.9°), which may cause the Zr-N1 bond (2.324(6) Å) slightly longer than the other Zr-N bonds (2.266(6) - 2.294(5)Å).

The eclipsed conformation of the two porphyrin rings and the concomitant eclipsed configuration of one of the Zr-O bonds with respect to a Zr-N bond commonly found in **1** and **2** strongly suggest that such conformation for the $N_4ZrO_3ZrN_4$ unit be stabilized by d_π-p_π interactions between the Zr atoms and the O and N atoms. A theoretical investigation14) is underway to gain the better understanding of such unusual geometry and bonding.

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References

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8) The suspension of THF (ca. 20 ml) containing $Zr(OEP)Cl_2$ (64.5 mg, 92.8 µmol) and $Tl_2(C_2B_9H_{11})$ (52.8 mg, 97.6 µmol) was stirred vigorously for 2h at room temperature under N_2. The reaction mixture was then filtered and the filtrate was evaporated to dryness under a reduced pressure. The residue was redissolved in CH_2Cl_2 and allowed to cool to -20 °C overnight. Red solid was filtered and dried in vacuo. Yield: 32.7 mg (49 %). UV/VIS (CH_2Cl_2): λ_{max} [nm] (log ε) = 390 (5.12), 532 (3.87), 568 (4.05); IR (KBr): ν[cm^{-1}] = 3652 (w, O-H), 2514 (vs, B-H); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.63 (s, 8H; meso H), 3.84 (q, 32H; CH_2), 1.72 (t, 48H; CH_3), -7.72 (s, 3H; OH); $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$, referenced to external $BF_3{\cdot}Et_2O$ at 0 ppm): δ = -11.44 (2B), -17.41 (3B), -22.47 (2B), -33.58 (1B), -38.20 (1B); MS (FAB, 70 eV): *m/z* 1431 (MH^+); Anal. Found: C, 59.48; H, 6.81; N, 7.50 %. Calcd for $C_{74}H_{103}N_8B_9O_3Zr_2{\cdot}CH_2Cl_2$: C, 59.36; H, 6.99; N, 7.39 %.

9) Crystal data for **1**: $C_{74}H_{103}N_8B_9O_3Zr_2$, M = 1432.44, monoclinic, *C2/m* (No. 12), a = 19.185 (7), b = 21.626 (4), c = 9.396 (3) Å, b = 101.03 (1)°, V = 3826 (2) Å^3, Z = 2, ρ_{calcd} = 1.243 g cm^{-3}, μ = 3.15 cm^{-1}, temp = 23 °C, $R(F)$ = 0.048, $R_\omega(F)$ = 0.056 for 249 variables and 2343 unique data with $I > 3\sigma(I)$; crystal data for **2**: $C_{88}H_{58}N_8O_3Zr_2{\cdot}C_6D_6$, M = 1542.10, orthorhombic, *Fdd*2 (No. 43), a = 25.526 (2), b = 39.546 (5), c = 14.796 (2) Å, V = 14936 (3) Å^3, Z = 8, ρ_{calcd} = 1.369 g cm^{-3}, μ = 3.30 cm^{-1}, temp = 23 °C, $R(F)$ = 0.040, $R_\omega(F)$ = 0.043 for 483 variables and 2471 unique data with $I > 3\sigma(I)$; Enraf-Nonius CAD4 diffractometer, graphite-monochromated Mo Kα radiation (λ (Mo Kα_1) = 0.70926 Å). The structures were solved by a combination of Patterson and difference Fourier methods and refined by full-matrix least-squares methods. Hydrogen atoms of the hydroxo could not be located and were therefore not included. Other hydrogen atom positions were idealized and included as fixed contributions.

10) Primed, double-primed and triple-primed atoms are related to the corresponding unprimed atoms by the twofold, plane, and inversion symmetries, respectively.

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13) Crystals of **2** were obtained adventitiously when n-hexane was allowed to diffuse into the C_6D_6 solution of $Zr(TPP)Me_2$ in an NMR tube; UV/VIS (CH_2Cl_2): λ_{max} [nm] (log ε) = 408 (5.07), 540 (4.34); IR (KBr): ν[cm^{-1}] = 3740 (w, O-H); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.63 (s, 16H; pyrrole H), 7.58 (s, 8H; Ph), 7.38 (s, 24H; Ph), 7.32 (s, 8H; Ph), -6.73 (s, 2H; OH); MS (FAB, 70 eV): *m/z* 1455 (MH^+); Anal. Found: C, 72.63 ; H, 4.37; N, 7.32 %. Calcd for $C_{88}H_{58}N_8O_3Zr_2$: C, 72.49; H, 4.02; N, 7.69 %.

14) A theoretical study on $O_3Nb_2(TPP)_2$ with a staggered conformation was reported; K. Tatsumi and R. Hoffmann, *J. Am. Chem. Soc.*, **103**, 3328 (1981).

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