

High-vacuum pyrolysis of Zr(2,3,7,8,12,13,17,18-octaethylporphyrin)(PhC≡CPh) as a route to novel Zr species: X-ray structure of a hetero-triply bridged species, [(OEP)Zr(μ-Cl)]₂(μ-O).

James P. Collman, Roman Boulatov, Geoffrey B. Jameson, Vipin Narang
Department of Chemistry, Stanford University, Stanford, CA 94305 and Centre for Structural Biology, Institute of Fundamental Sciences, Massey University, Palmerston North (New Zealand).

Supplemental Information.

Synthesis of [Zr(OEP)(μ-OH)]₂(μ-O) and [Zr(OEP)(μ-O)]₂ Formation of these species was previously reported, although ¹H-NMR was given only for the former complex and only in CDCl₃¹. The hydroxo-bridged dimer was obtained by hydrolysis of Zr(OEP)Cl₂ in a pyridine-CH₂Cl₂ (1:1) solution, similar to a method used for synthesis of other Zr-O-Zr bridged species. Zr(OEP)Cl₂ (10 mg) was dissolved in anhydrous pyridine (4 mL), diluted with anhydrous CH₂Cl₂ (4 mL) and exposed to air. After 1 day, the solvents were removed under vacuum, the residue, which mainly contained [Zr(OEP)(μ-OH)]₂(μ-O) and small amounts of [Zr(OEP)(μ-O)]₂ and Zr(OEP)Cl₂ as judged by ¹H NMR, was treated with C₆H₆ to remove the last 2 components. The hydroxo-bridged dimer is only sparingly soluble in benzene. ¹H NMR (anhydrous C₆D₆): 9.52 (s, 4 H, *meso*-), 3.88 (m, 8 H, CH₂), 3.75 (m, 8 H, CH₂), 1.63 (t, 7.5 Hz, 24 H, CH₃), -6.92 (s, 2 H, μ-OH); the position of the *meso*-protons is greatly affected by the presence of pyridine, which significantly increases solubility of the complex in benzene (δ_{meso} = 9.97 ppm if *ca.* 3 eq. pyridine are present) or by H₂O. These compounds also cause broadening of the μ-OH resonances, but do not change its position. [Zr(OEP)(μ-OH)]₂(μ-O) converts to [Zr(OEP)(μ-O)]₂ in 30 hours under dynamic vacuum (5 mTorr) at room temperature. This complex is significantly more soluble in benzene, which was used to separate it from unreacted [Zr(OEP)(μ-OH)]₂(μ-O). ¹H NMR (C₆D₆): 9.71 (s, 4 H, *meso*-), 3.83 (m, 8 H, CH₂), 3.67 (m, 8 H, CH₂), 1.67 (t, 7 Hz, 24 H, CH₃). IR (KBr): 696 cm⁻¹ (Zr-O-Zr) +ESI/MS (pyridine): 1279.6 (cluster, M-H⁺); calcd for C₇₂H₈₉O₂Zr₂: 1279.5 (cluster). The complex reverts to [Zr(OEP)(μ-OH)]₂(μ-O) in wet solvents.

X-ray structure determination of [Zr(OEP)(μ-Cl)]₂(μ-O) (3) X-ray diffraction data were collected from a very thin plate, leading to a rather weak data set that did not extend beyond 1.05 Å in resolution. Thus, restraints were applied to the anisotropic displacement parameters of all non-carbon atoms in least-squares refinements with SHELXL-97 (DELU 0.01 and ISOR 0.005). See Table S1 details of crystal, data collection and refinement parameters.

Table S1. Crystallographic data for [Zr(OEP)(μ-Cl)]₂(μ-O) (3).

Empirical Formula	C ₇₂ H ₈₈ Cl ₂ N ₈ O Zr ₂
Formula Weight	1334.84
Crystal Dimensions (mm)	0.26 x 0.26 x 0.007

Lattice Parameters	a = 18.836(4) Å
	b = 15.084(4) Å
	c = 23.170(5) Å
	$\alpha = 90^\circ$
	$\beta = 100.016(5)^\circ$
	$\gamma = 90^\circ$
	V = 6483(3) Å ³
Space Group	P2 ₁ /c (#14)
Z value	4
D _{calc}	1.37 g/cm ³
R (wR ₂)*	0.0621 (0.1593)
Goodness of Fit Indicator	0.712
Crystal color, habit	Red, very thin plate
Crystal system	Monoclinic
Lattice type	Primitive
Reflections used for unit cell determination (2 θ range)	1261 (3.65° < 2 θ < 39.6°)
F ₀₀₀	2792
μ (Mo-K α)	4.55 cm ⁻¹
Diffractometer	Siemens SMART CCD
Radiation	Mo-K α ($\lambda = 0.7069$ Å); graphite monochromated
Temperature	-94 ± 1 °C
Scan type/slicing	$\omega/0.3^\circ$
2 θ_{\max}	39.6°
Reflections measured	18203 (total); 6153 (unique, R _{int} = 0.088, I > 1 σ (I))
Corrections	Lorentz, polarization, absorption
Refinement	Full-matrix least-square on F ²
Function minimized [†]	$\sum w(F_o^2 - F_c^2)^2$
Anomalous dispersion	all non-hydrogen atoms
Variables/restraints	763/696
Reflection/parameter ratio	7.7
Max shift/ σ in final cycle	0.003

$$* R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = [\sum (w (F_o^2 - F_c^2)^2) / \sum w(F_o^2)]^{1/2}$$

$$^\dagger \text{Weight} = 1/[\sigma^2(F_o^2) + (0.0576p)^2] \text{ where } P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$$

References:

1. Brand, H.; Arnold, J. *Organometallics* **1993**, *12*, 3655 – 3665.