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Novel Disulfido- and Diselenido-Bridged Zirconium and Hafnium Porphyrin Dimers with Unusual Coordination Geometries: [M(TPP)]$_2$(μ-η^2-Q$_2$)$_2$ (M = Zr, Hf; Q = S, Se)

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Introduction

Transition metal−chalcogen complexes are of interest not only with regard to their structures and reactivity but also because of their potential uses in catalysis and other applications.[1,2] While the chemistry of transition metal porphyrin complexes having oxo[3] or peroxo[4] ligands has been studied quite extensively, that of the corresponding sulfido and selenido complexes still remains undeveloped.[5,6] Recently, we and others prepared M(por)Cl$_2$ [M = Zr,[7,8] Hf;[9] por = 2,3,7,8,12,13,17,18-octaethylporphyrinate (OEP) and 5,10,15,20-tetraphenylporphyrinate (TPP)] and demonstrated their use as precursors for new coordination and organometallic porphyrin complexes. Continuing with that work, we now report the synthesis and X-ray crystal structures of [M(TPP)]$_2$(μ-η^2-Q$_2$)$_2$ (M = Zr, Hf; Q = S, Se) having unusual coordination geometries. These are the first examples of dimeric metalloporphyrin chalcogenide complexes.

Table 1. Selected Bond Distances (Å) and Angles (deg) of **1**

Distances					
Zr−S1	2.656(3)	Zr−S1′	2.664(3)	S1−S2	2.070(4)
Zr−S2	2.651(3)	Zr−S2′	2.657(3)	S1′···S2′	3.298(4)
Angles					
S1−Zr−S2	45.9(1)	S1′−Zr−S2′	45.80(9)		
S1−Zr−S2′	76.7(1)	S1−Zr−S1′	94.4(1)		
S1′−Zr−S2	76.7(1)	S2−Zr−S2′	94.13(9)		

Results and Discussion

The reaction of M(TPP)Cl$_2$ (M = Zr, Hf) with 1 equiv of Li$_2$Q$_2$ (Q = S, Se) at room temperature yielded a class of compounds, the formula of which is consistent with M(TPP)(Q$_2$) (M = Zr, Hf; Q = S, Se) as the major product. The ^{1}H NMR spectra of these compounds are nearly identical, indicating that they have the same structures. One interesting aspect of the ^{1}H NMR spectra is two well-separated singlet peaks for the pyrrole β protons. These peaks are in sharp contrast to the report of only one singlet peak for the pyrrole β protons in the dichalogenide complexes Ti(TTP)(η^2-Q$_2$) (Q = S, Se).[5a,b] Moreover, the pyrrole β proton signals in the spectra of our new compounds are shifted to higher field compared to the single peak for the titanium dichalcogenide complexes, which suggests a dimeric structure for our new compounds. The mass spectral data for these compounds are also consistent with a dimer formula [M(TPP)]$_2$(μ-η^2-Q$_2$)$_2$ (M = Zr, Hf; Q = S, Se).

$$\begin{array}{l} \mathrm{M(TPP)Cl_2} + \mathrm{Li_2Q_2} \rightarrow [\mathrm{M(TPP)}]_2(\mu\text{-}\eta^2\text{-}\mathrm{Q_2})_2 \\ \qquad\qquad\qquad\qquad\quad \mathbf{1}\text{: } \mathrm{M = Zr, Q = S} \\ \qquad\qquad\qquad\qquad\quad \mathbf{2}\text{: } \mathrm{M = Zr, Q = Se} \\ \qquad\qquad\qquad\qquad\quad \mathbf{3}\text{: } \mathrm{M = Hf, Q = S} \\ \qquad\qquad\qquad\qquad\quad \mathbf{4}\text{: } \mathrm{M = Hf, Q = Se} \end{array}$$

X-ray crystal structure determinations of **1** and **4** confirmed the dimeric nature of these compounds. Since the crystals of **1** and **4** are isomorphous, the discussion of the structures is mainly focused on **1**. The structure of the zirconium disulfide complex **1** is shown in Figure 1, and selected bond distances and angles of **1** are given in Table 1. The molecule possesses an inversion center located at the midpoint of the two Zr atoms. Each zirconium atom is coordinated by four N atoms of the porphyrin and two doubly bidentate μ-S$_2^{2-}$ ligands. The geometry of the Zr$_2$S$_4$ core is a distorted octahedron. The coordination mode M$_2$(μ-η^2-S$_2$)$_2$ is quite rare; in fact, it has been observed only once in [(η^5-C$_5$Me$_5$)$_2$Fe$_2$S$_4$](PF$_6$)$_2$.[10] Both of the μ-S$_2^{2-}$ ligands lie in a plane parallel to the two porphyrin macrocycles. The zirconium atom is 1.044(4) Å above the porphyrin N$_4$ plane and 1.808(2) Å below the S$_4$ plane with a Zr···Zr separation of 3.616(3) Å. The Zr−S1 and Zr−S2 distances are 2.656(3) and

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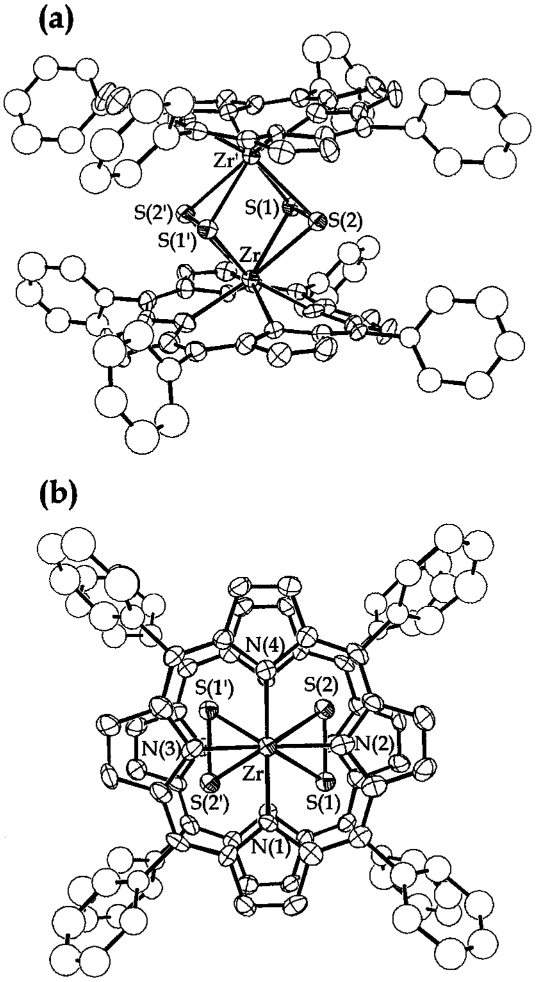

Figure 1. Structure of $[Zr(TPP)]_2(\mu\text{-}\eta^2\text{-}S_2)_2$ (**1**): (a) side view; (b) top view.

2.651(3) Å, respectively, with an S1−Zr−S2 bond angle of 45.9(1)°. The Zr−N bond distances range from 2.234(9) to 2.285(9) Å, with an average value of 2.26(2) Å. One interesting feature of the structure is the almost perfect eclipsing of the two porphyrin rings (Figure 1b): the torsion angle N1−Zr−Zr−N4′ is nearly zero. Such an eclipsed geometry for two porphyrin macrocycles is unusual although not unprecedented; it has been observed in tri-oxygen-atom-bridged Zr or Hf porphyrin dimers such as $[M(TPP)]_2(\mu\text{-}OH)_3$ or $[M(TPP)]_2(\mu\text{-}O)(\mu\text{-}OH)_2$ (M = Zr,[7b] or Hf[9c]). The two $\mu\text{-}S_2^{2-}$ ligands are oriented in such a way that the plane containing Zr, N2, and N3 bisects the S1−S2 and S1′−S2′ bonds. The S1-S2 bond distance (2.070(4) Å) is slightly longer than that found in $[(\eta^5\text{-}C_5Me_5)_2Fe_2S_4](PF_6)_2$ (1.983(1) Å).[10] The distance between S1 and S2′ is too long (3.298(4) Å) to be considered a chemical bond. Metric parameters of **1** and **4** are compared in Table 2. The larger ionic radius of Se vs S is responsible for the larger M···M distance and Q−M−Q angle in **4** than those found in **1**.

The above-mentioned two separated singlet resonances for the pyrrole β protons in the ^{1}H NMR spectra of these compounds demonstrate that their solid state structures remain intact in solution and the rotation of the porphyrin macrocycles with respect to the M_2Q_4 core is slow on the NMR time scale at room temperature. These results are in sharp contrast to the tri-oxygen-atom-bridged Zr and Hf porphyrin dimers $[M(TPP)]_2(\mu\text{-}OH)_3$ and $[M(TPP)]_2(\mu\text{-}O)(\mu\text{-}OH)_2$ (M = Zr,[7b] Hf[9c]), in whose spectra only one singlet is observed for the pyrrole β protons even at −50 °C, and suggest that the rotation of the porphyrin rings with respect to the $M{-}O_3{-}M$ core is fast on the NMR time scale. The rotational barrier of the porphyrin rings with respect to the $M{-}(Q_2)_2{-}M$ core could not be measured because of the poor solubility of these compounds in organic solvents other than $CHCl_3$.

Table 2. Comparison of Some Structural Features of **1** and **4** (Distances, Å; Angles, deg)[a]

	1	**4**
M···M	3.616(3)	3.733(4)
M···N_4 plane	1.044(4)	1.081(3)
M···Q_4 plane	1.808(2)	1.867(2)
M−N_{av}	2.26(2)	2.23(9)
Q1−Q2	2.070(4)	2.38(1)
Q1−Q2′	3.298(4)	3.420(8)
Q1−M−Q2′	45.9(1)	50.2 (2)

[a] M = Zr and Q = S for **1** and M = Hf and Q = Se for **4**.

In summary, we have synthesized and structurally characterized the novel metalloporphyrin chalcogenide complexes $[M(TPP)]_2(\mu\text{-}\eta^2\text{-}Q_2)_2$ (M = Zr, Hf; Q = S, Se). These compounds not only represent the first examples of dimeric metalloporphyrin chalcogenide complexes but also exhibit unusual coordination geometry around the metal centers. These results are in contrast to those for Ti porphyrins, which form the mononuclear disulfido and diselenido complexes $Ti(por)(\eta^2\text{-}Q_2)$ (Q = S, Se). The preference of Zr and Hf for a coordination number higher than that of Ti appears to be responsible for the formation of dichalcogen-bridged dimers in the case of Zr and Hf porphyrins. The reactivities of these dichalcogen-bridged porphyrin dimers are currently under investigation.

Experimental Section

Chemicals. All chemicals were of reagent grade and were used without further purification except as noted below. Argon was purified by passage through successive columns of activated molecular sieves 13X (Aldrich) and Ridox (Fisher). $Zr(TPP)Cl_2$[7a] and $Hf(TPP)Cl_2$[9a] were prepared by literature procedures. All solvents were distilled from their sodium benzophenone ketyl solutions (toluene, THF, and hexanes) or from P_2O_5 ($CHCl_3$) under an atmosphere of nitrogen. $CDCl_3$ was dried over CaH_2 and purified by vacuum transfer.

Methods and Instruments. All manipulations of oxygen- and water-sensitive materials were performed either in a Vacuum Atmospheres glovebox under a nitrogen atmosphere or in Schlenkware under purified argon. UV-visible spectra were recorded on a Hewlett-Packard 8542A or a Shimadzu UV-265FS spectrometer. ^{1}H NMR spectra were obtained on a Bruker AM 300 or a JEOL GSX-270 spectrometer. Chemical shifts are referenced to tetramethylsilane at 0 ppm. Infrared spectra were recorded on a Bomem Michelson 100 or a Hitachi 295 spectrometer. Mass spectra for **1** and **2** were obtained on a JEOL SX-102 spectrometer. Elemental analyses for **1** and **2** were obtained on a Yanagimoto Model CHN Corder MT-2. Mass spectrometry for **4** and elemental analyses for **3** and **4** were performed by the Korea Basic Science Center.

Syntheses. (a) $[Zr(TPP)]_2(\mu\text{-}\eta^2\text{-}S_2)_2$ (1).[11] A solution of $Zr(TPP)Cl_2$ (209 mg, 0.27 mmol) in THF (25 mL) was transferred to a suspension of Li_2S_2 (66 mg, 0.85 mmol, prepared by the reaction of lithium metal with elemental sulfur in liquid ammonia) in THF (10 mL) and stirred for 12 h under argon. The solution was evaporated to dryness, and the solid was extracted with toluene (3 × 10 mL). Removal of the solvent gave purple microcrystals of **1** (277 mg, 67%). Analytically pure material was recrystallized from THF/hexanes. Anal. Calcd for $C_{88}H_{56}N_8S_4Zr_2$: C, 68.80; H, 3.68; N, 7.30. Found: C, 68.42;

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Table 3. Crystal and Refinement Data for **1**·$4C_4H_8O$ and **4**·$2CHCl_3$

	1·$4C_4H_8O$	**4**·$2CHCl_3$
formula	$C_{88}H_{56}N_8S_4Zr_2\cdot 4C_4H_8O$	$C_{88}H_{56}N_8Se_4Hf_2\cdot 2CHCl_3$
fw	1824.50	2137.06
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	13.031(6)	12.917(15)
b, Å	23.720(10)	23.916(2)
c, Å	15.258(8)	15.099(16)
β, deg	102.99(4)	102.40(5)
V, Å^3	4596(4)	4556(7)
Z	2	2
temp, °C	20	23
d(calcd), g/cm^3	1.319	1.548
λ(Mo Kα), Å	0.710 73	0.710 73
linear abs coeff, cm^{-1}	3.75	40.38
2θ limit, deg	40	42
no. of data collected	4522	4840
no. of unique data	2430 ($I > 2\sigma(I)$)	1579 ($I > 3\sigma(I)$)
no. of variables	415	252
R factor	R1^a ($I > 2\sigma(I)$) = 0.067 wR2^a (all) = 0.218	R^b ($I > 3\sigma(I)$) = 0.10 $R_w{}^b$ (all) = 0.13

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o{}^2) + (0.0757P)^2 + 9.1430P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 4F_o{}^2/\sigma^2(F_o{}^2)$; $\sigma^2(F_o{}^2) = [\sigma^2(I) + (pF_o{}^2)^2]^{1/2}$, $p = 0.04$.

H, 3.85; N, 6.97. ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C): δ 8.53 (s, 8H, H_β), 8.31 (s, 8H, H_β), 8.05 (d, 8H, $H_{o'}$), 7.86 (t, 8H, $H_{m'}$), 7.75 (t, 8H, H_p), 7.71 (d, 8H, H_o), 7.58 (t, 8H, H_m). UV−vis (THF, nm): 414 (Soret), 543. IR (CsI, cm^{-1}): 377 (w) (Zr−S). MS (FAB): *m/z* 1534 ($[Zr(TPP)]_2S_4{}^+$), 1471 ($[Zr(TPP)]_2S_2{}^+$), 767 ($Zr(TPP)S_2{}^+$), 735 ($Zr(TPP)S^+$).

(b) $[Zr(TPP)]_2(\mu\text{-}\eta^2\text{-}Se_2)_2$ (2). The selenium complex **2** was prepared by using lithium diselenide and the same procedure as for the sulfur complex **1** (293 mg, 63%). Anal. Calcd for $C_{88}H_{56}N_8Se_4Zr_2\cdot C_4H_8O$: C, 61.52; H, 3.60; N, 6.24. Found: C, 61.44; H, 3.67; N, 5.84. ^{1}H NMR (270 MHz, $CDCl_3$, 25°C): δ 8.56 (s, 8H, H_β), 8.33 (s, 8H, H_β), 8.13 (d, 8H, $H_{o'}$), 7.86 (t, 8H, $H_{m'}$), 7.79 (t, 8H, H_p), 7.71 (d, 8H, H_o), 7.60 (t, 8H, H_m). UV−vis (THF, nm): 415 (Soret), 534. IR (CsI, cm^{-1}): 380 (w) (Zr−Se). MS (FAB): *m/z* 1725 ($[Zr(TPP)]_2Se_4{}^+$), 862 ($Zr(TPP)Se_2{}^+$), 783 ($Zr(TPP)Se^+$).

(c) $[Hf(TPP)]_2(\mu\text{-}\eta^2\text{-}S_2)_2$ (3). Addition of $LiEt_3BH$ (0.7 mL, 0.70 mmol, 1.0 M THF solution) to sulfur powder (22.3 mg, 0.69 mmol) under dry argon with stirring resulted in gas evolution for 2 min. The solution immediately turned to a clear yellow solution, which was stirred for another 10 min. To this solution was added a THF solution of $Hf(TPP)Cl_2$ (100 mg, 0.12 mmol) dropwise with stirring to give a dark brownish red solution. After 12 h of stirring, the resulting purple microcrystalline solid was filtered off, washed with THF, and dried in vacuo, yielding **3** (35 mg, 36%). Analytically pure material was recrystallized from $CHCl_3$/hexanes. Anal. Calcd for $C_{88}H_{56}N_8S_4Hf_2\cdot {}^1/_2CHCl_3$: C, 60.04; H, 3.22; N, 6.33; S, 7.24. Found: C, 59.99; H, 3.41; N, 6.17; S, 7.27. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ 8.54 (s, 8H, H_β), 8.28 (s, 8H, H_β), 8.04 (d, 8H, $H_{o'}$), 7.85 (t, 8H, $H_{m'}$), 7.76 (t, 8H, H_p), 7.74 (d, 8H, H_o), 7.57 (t, 8H, H_m). UV−vis ($CHCl_3$, nm): 416 (Soret), 538. IR (KBr, cm^{-1}): 380 (w) (Hf−S). MS (FAB): *m/z* 1712 ($[Hf(TPP)]_2S_4{}^+$), 1649 ($[Hf(TPP)]_2S_2{}^+$).

(d) $[Hf(TPP)]_2(\mu\text{-}\eta^2\text{-}Se_2)_2$ (4). The selenium complex **4** was prepared by using lithium diselenide and the same procedure as for the sulfur complex **3** (50 mg, 45%). Anal. Calcd for $C_{88}H_{56}N_8Se_4Hf_2\cdot C_4H_8O$: C, 56.07; H, 3.28; N, 5.69. Found: C, 56.40; H, 3.05; N, 5.67. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ 8.57 (s, 8H, H_β), 8.31 (s, 8H, H_β), 8.13 (d, 8H, $H_{o'}$), 7.85 (t, 8H, $H_{m'}$), 7.75 (t, 8H, H_p), 7.71 (d, 8H, H_o), 7.57 (t, 8H, H_m). UV−vis ($CHCl_3$, nm): 416 (Soret), 538; IR (CsI, cm^{-1}): 378 (w) (Hf−Se).

X-ray Crystal Structure Determinations. X-ray-quality crystals of **1** and **4** were grown by slow diffusion of hexanes into a THF solution of **1** and a $CHCl_3$ solution of **4**, respectively. The quality of the crystals of **4** was marginal. A crystal was sealed in a sealed capillary tube with the mother liquor. Intensity data were collected on a Rigaku AFC7R for **1** and on an Enraf-Nonius CAD4 diffractometer for **4**, using graphite-monochromated Mo Kα radiation at room temperature. Unit cell parameters were determined by least-squares refinement of 25 reflections. The intensities of three standard reflections, measured every 3 h of X-ray exposure, showed no systematic changes. The intensity data were corrected for Lorentz and polarization effects, and empirical absorption corrections (XABS2[12] (**1**) or DIFABS[13] (**4**)) were also applied. For solution and refinement of **1**, the programs SHELXS-86 and SHELXL-93 were used.[14] All calculations for **4** were carried out with the Enraf-Nonius MolEN package.[15] The structure of **4** was solved by a combination of Patterson and difference Fourier methods, and both structures were refined by full-matrix least-squares methods. The Zr, S, and 24 atoms of the porphyrin ligands in **1** were refined anisotropically. The Hf and Se atoms in **4** were also refined anisotropically. The positions of hydrogen atoms (except for those of the solvate molecules) were calculated (C−H = 0.96 Å) and were included as fixed contributions to the structure factors. Each hydrogen atom was assigned an isotropic thermal parameter 1.2 times that of the atom to which it was attached. Scattering factors for H were obtained from Stewart et al.,[16] and those for other atoms were taken from ref 17. Crystal and refinement data for **1** and **4** are summarized in Table 3.

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Supporting Information Available: Tables of crystallographic details, atomic coordinates and equivalent isotropic thermal parameters, bond distances and angles, and anisotropic thermal parameters for **1** and **4** (13 pages). Ordering information is given on any current masthead page.

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