Synthesis, Characterization, and Structure of (μ-Sulfido)bis[(octaethylporphyrinato)ruthenium(III)], $[Ru(OEP)]_2S$

Gordon T. Yee,* Bruce C. Noll,
Daniel K. C. Williams, and Scott P. Sellers

Department of Chemistry and Biochemistry,
University of Colorado, Boulder, Colorado 80309

Received December 20, 1996

Introduction

It has long been known that, in solution, the reaction of many different synthetic square planar (porphyrinato)iron(II) complexes with molecular oxygen yields the corresponding dinuclear five-coordinate iron complex, (μ-oxo)bis[(porphyrinato)iron(III)].[1] The crystal structures of approximately a dozen examples utilizing a variety of porphyrin and porphyrin-like macrocycles have been reported[2] and, with one exception,[3] show nearly linear (175 ± 5°) Fe−O−Fe bonding. This geometry is not predicted by theory based on the electronic configuration of the Fe(III)−O−Fe(III) core but has been ascribed to a weak preference by this fragment for the bent structure which is overwhelmed by the desire to minimize ligand−ligand $\pi-\pi$ repulsions in the linear arrangement.[4] In the corresponding less sterically restrictive salicylideneethylenediimine (salen) complex, $[Fe(salen)]_2O{\cdot}(py)_2$,[5] the Fe−O−Fe bond angle has been determined by crystallography to be 139°.

No ruthenium porphyrin homologues of this structure have been reported to date. In their reactions with oxygen, coordinatively unsaturated ruthenium(II) porphyrins are always isolated with the metal in either the +4 or the +6 oxidation state. For instance, (octaethylporphyrinato)ruthenium(II) dimer, $[Ru(OEP)]_2$, reacts with molecular oxygen in solution to form (μ-oxo)bis[hydroxo(octaethylporphyrinato)ruthenium(IV)], $[Ru(OEP)(OH)]_2O$.[6] This structurally characterized complex possesses a capping hydroxide ligand in the sixth coordination site of each ruthenium.[7] Several related complexes exist in which the capping hydroxy ligand is replaced by a halogen or an alkoxide ligand.[8] In each of these structures, the Ru−O−Ru bond angle is 180°, in accordance with predictions for d^4-d^4 species.[4] Sterically hindered ruthenium porphyrin complexes such as (*meso*-tetramesitylporphyrinato)ruthenium(II) and its carbon monoxide adduct, which apparently cannot form the μ-oxo structure, instead form a ruthenium(VI) *trans*-dioxo complex, $Ru(TMP)(O)_2$.[9] In this contribution, we report what may be considered the closest available homologue to $[Fe(OEP)]_2O$ in ruthenium chemistry, (μ-sulfido)bis[(octaethylporphyrinato)ruthenium(III)], $[Ru(OEP)]_2S$.

Experimental Section

All chemicals were obtained from the Aldrich Chemical Co. All manipulations were carried out in a Braun inert atmosphere glovebox maintained at 5 ppm O_2 or less. The thermolysis was carried out on an oil diffusion-pumped vacuum line kept at 10^{-5} Torr or better. Visible spectra were recorded on a Perkin-Elmer Lambda 9 UV/vis/nIR spectrophotometer. ^1H NMR spectra were obtained on a Bruker AM 400 MHz. Chemical shifts are reported relative to benzene ($\delta = 7.15$ ppm). Electrospray (ESI) and fast atom bombardment (FAB) mass spectrometry were obtained on PE/Sciex API-III tandem mass spectrometer and VG 7070 EQHF mass spectrometer, respectively. Elemental analyses were performed by Supersun Technology, Stony Brook, NY.

Materials. Free-base octaethylporphyrin[10] and bis[(octaethylporphyrinato)ruthenium(II)][11] were prepared as described in the literature. Benzene, diethyl ether, and hexane were distilled from sodium benzophenone ketyl and stored in the glovebox. Benzene-d_6 was vacuum transferred from sodium/potassium benzophenone ketyl. Ethylene sulfide was subjected to three successive freeze−pump−thaw cycles but was not otherwise purified. Florisil (activated magnesium silicate) was degassed at room temperature at 10^{-5} Torr overnight.

Synthesis of $Ru(OEP)(SC_2H_4)_2$ (1). To a solution of $[Ru(OEP)]_2$ (39 mg, 31 μmol) in 20 mL of benzene was added three drops (∼2 mmol) of ethylene sulfide. The solution immediately turned from green to red. Removal of the solvent and excess ethylene sulfide under vacuum and chromatography of the product on Florisil, eluting with 10:1 benzene/diethyl ether, resulted in an analytically pure, air-sensitive material. Yield: 36 mg (77%). Anal. Calcd for $C_{40}H_{52}N_4RuS_2$: C, 63.71; H, 6.95; N, 7.43; S, 8.50. Found: C, 63.80; H, 7.08; N, 7.46; S, 9.23. ^1H NMR (C_6D_6) δ 9.76 (s, 4H, H_{meso}), 3.92 (q, 16H, 7.6 Hz, $H_{methylene}$), 1.94 (t, 24H, 7.6 Hz, H_{methyl}), −2.00 (d, 4H, 5 Hz), −3.35 (d, 4H, 5 Hz). UV−vis (benzene) (λ_{max}, nm): 408, 500, 527. Crystals of this compound suitable for X-ray crystallography were grown by dissolving the complex in benzene and carefully layering on hexane.

Synthesis of $[Ru(OEP)]_2S$ (2). $Ru(OEP)(SC_2H_4)_2$ (36 mg, 48 μmol) was dissolved in benzene and freeze-dried at 0 °C to an amorphous powder on the vacuum line overnight. The sample was then heated under vacuum in a sand bath at 130 °C for 3 h, during which time the solid changed from red to purple. The sample was returned to the glovebox and chromatographed on Florisil, eluting with 10:1 benzene/diethyl ether. Yield: 22 mg (71%). ^1H NMR (C_6D_6): δ 9.00 (s, 8H, H_{meso}), 3.90 (m, 16H, 8 Hz, $H_{methylene}$), 3.62 (m, 16H, 8 Hz, $H_{methylene}$), 1.62 (t, 48H, 8 Hz, H_{methyl}). UV−vis (benzene) (λ_{max}, nm): 393, 418 (s), 528. We were unable to obtain satisfactory elemental analysis on this compound, perhaps due to its air-sensitivity. However, mass spectral analyses were consistent with this formulation. The most intense ion in the molecular ion cluster was calculated to be 1300.5, and M^+ (found) was 1300.6 (ESI) and 1300.7 (FAB). Crystals of this compound suitable for X-ray crystallography were grown by dissolving it in benzene and carefully layering on hexane.

Interestingly, **2** may also be prepared as a minor product from the reaction of $[Ru(OEP)]_2$ with carbon disulfide in benzene. The major product in this case is the previously identified thiocarbonyl complex, Ru(OEP)(CS)L, as determined by comparison of its pyridine adduct Ru(OEP)(CS)py to a published NMR spectrum.[12]

In the glovebox, $[Ru(OEP)]_2$ (50 mg, 40 μmol) was dissolved in 15 mL of benzene in a 25 mL round bottom flask. The flask was sealed with a rubber stopper and brought out of the glovebox. Degassed carbon disulfide (1 mL, 17 mmol) was added by syringe and the reaction stirred overnight. The solvent was removed by vacuum and the residue

---

(1) Hoffman, A. B.; Collins, D. M.; Day, V. W.; Fleischer, E. B.; Srivastava, T. S.; Hoard, J. L. *J. Am. Chem. Soc.* **1972**, *94* , 3620−3626.

(2) Cheng, B.; Hobbs, J. D.; Debrunner, P. G.; Erlebacher, J.; Shelnutt, J. A.; Scheidt, W. R. *Inorg. Chem.* **1995**, *34*, 102 and references therein.

(3) Lausmann, M.; Zimmer, I.; Lex, J.; Lueken, H.; Wieghardt, K.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 736.

(4) Tatsumi, K.; Hoffman, R. *J. Am. Chem. Soc.* **1981**, *103*, 3328.

(5) Gerlock, M.; McKenzie, E. D.; Towl, A. D. C. *J. Chem. Soc. A* **1969**, 2850−2858.

(6) Collman, J. P.; Barnes, C. E.; Collins, T. J.; Brothers, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 7030.

(7) Masuda, H.; Taga, T.; Osake, K.; Sugimoto, H.; Mori, M.; Ogoshi, H. *J. Am. Chem. Soc.* **1981**, *103*, 2199.

(8) Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Mori, M.; Ogoshi, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3887.

(9) (a) Camenzind, M. J.; James, B. R.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1986**, 1137. (b) Groves, J. T.; Quinn, R. *Inorg. Chem.* **1984**, *23*, 3844−3846.

(10) Sessler, J. L.; Mazaffari, A.; Johnson, M. R. *Org. Synth.* **1992**, *70*, 68.

(11) (a) Collman, J. P.; Garner, J. M.; Woo, L. K. *J. Am. Chem. Soc.* **1989**, *111*, 8141. (b) Collman, J. P.; Barnes, C. E.; Swepston, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 3500.

(12) Smith, P. D.; Dolphin, D.; James, B. R. *J. Organomet. Chem.* **1981**, *208*, 239.

S0020-1669(96)01511-X CCC: $14.00

Table 1. Crystallographic Data for Ru(OEP)(SC_2H_4)$_2$ and [Ru(OEP)]$_2$S

compound	Ru(OEP)(SC_2H_4)$_2$	[Ru(OEP)]$_2$S
empirical formula	$C_{40}H_{52}N_4RuS_2$	$C_{36}H_{44}N_4RuS_{0.50}$
formula mass	754.05	649.85
crystal system	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	*C*2/*c* (No. 15)
a, Å	9.1134(7)	25.8266(2)
b, Å	10.4966(8)	14.0882(2)
c, Å	10.9873(8)	17.55450(10)
α, deg	82.280(2)	90
β, deg	66.706(2)	93.8010(10)
γ, deg	68.220(2)	90
volume, Å^3	896.36(12)	6373.16(11)
Z	1	8
ρ_{calc}, mg m^{-3}	1.397	1.355
μ, mm^{-1}	0.588	0.556
transmission coeff	1.00 and 0.66	0.94 and 0.88
T, K	170(2)	123(2)
λ, Å	0.71073 (Mo Kα)	0.71073 (Mo Kα)
reflections collected	4440	12171
unique reflections	2796 (R(int) = 0.0625)	4575 (R(int) = 0.0435)
reflections observed	2208	3781
R index^a [$I > 2\sigma(I)$]	R1 = 0.0721,	R1 = 0.0354,
R indices^a (all data)	R1 = 0.1034, wR2 = 0.1918	R1 = 0.0510, wR2 = 0.0761
weighting coeffs^b	$a = 0.0703$, $b = 6.2381$	$a = 0.0167$, $b = 21.1483$
goodness of fit^c on F^2	1.090	1.089

^{a} $R1 = \sum||F_o - F_c||/\sum|Fo|$; $wR2 = \sum[w(F_o^2 - F_c^2)^2]/\sigma[w(F_o^2)^2]]^{1/2}$. ^{b} $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. ^{c} Goodness of fit $[\sum[w(F_o^2 - F_c^2)^2]/(M - N)]^1/_2$ where *M* is the number of reflections and *N* is the number of parameters refined.

returned to the glovebox. Chromatography on Florisil, eluting with benzene, yielded two products. The first, an orange band, was the thiocarbonyl complex; the second, a red band, was [Ru(OEP)]$_2$S as determined by ^{1}H NMR.

X-ray Crystallography. Crystals were handled under Exxon Paratone N oil. Both structure determinations utilized a Siemens Platform diffractometer equipped with a SMART CCD area detector, an LT-2A low-temperature apparatus, and a K760 X-ray generator at 1.75 kW. Data were corrected for Lorentz, polarization, and absorption effects. Structure solution and refinement was performed with the SHELXTL suite of programs.[13] A summary of the data collections is presented in Table 1. Full details of each experiment are available as Supporting Information.

The structure of **1** was solved by placing atom Ru at a crystallographic inversion center and calculating a difference Fourier map. This revealed the complete non-hydrogen structure. The asymmetric unit is one-half molecule. Hydrogen atoms were placed at calculated positions and allowed to ride on the position of the parent atom. Isotropic hydrogen thermal parameters were set to 1.2 times the equivalent isotropic value of the parent. The largest peak in the final difference map, with electron density of 1.337 e/Å^3, is located within 1 Å of Ru and is likely an artifact of absorption. No short intermolecular contacts were noted.

For **2**, structure solution via direct methods revealed all non-hydrogen atoms. Hydrogen atoms were placed at calculated geometry and allowed to ride on the position of the parent atom. Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen thermal parameters were set to 1.2× the equivalent isotropic value of the parent atom. The asymmetric unit is comprised of half of the molecule. Sulfur lies on a crystallographic 2-fold axis running through 0, *y*, 0.25. The two porphyrin planes form a 24° angle with respect to each other. A line passed through the Ru−S bond is 10.1° from the normal to the porphyrin plane. Closest approach between the two porphyrin planes, 3.24 Å, is C(12) to C(13A) by 2-fold rotation. Nearest intermolecular contacts are by inversion, which places neighboring planes parallel at 3.51 Å.

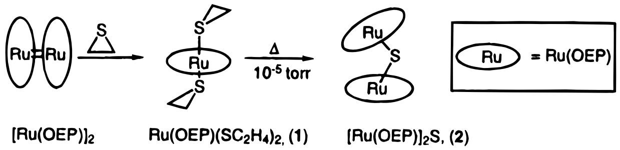

Figure 1. Synthesis of [Ru(OEP)]$_2$S (**2**).

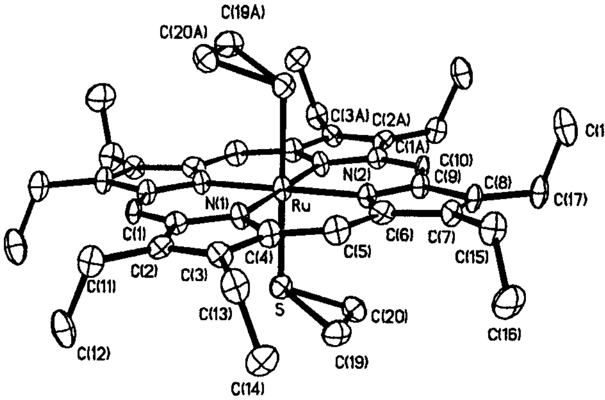

Figure 2. Thermal ellipsoid plot at 50% probability of Ru(OEP)(SC_2H_4)$_2$ (**1**). Hydrogen atoms have been omitted for clarity.

Results and Discussion

In our studies of ruthenium porphyrin complexes with organosulfur ligands, the synthon, [Ru(OEP)]$_2$, was allowed to react with ethylene sulfide in benzene (Figure 1). Removal of the solvent resulted in the isolation of *trans*-bis(ethylenesulfido)-[(octaethylporphyrinato)ruthenium(II)], Ru(OEP)(SC_2H_4)$_2$ (**1**), an air-sensitive red solid. The ^{1}H NMR spectrum displays a simple quartet and triplet pattern which may be ascribed to the peripheral ethyl groups on the porphyrin. From this, it may be inferred that there exists a plane of symmetry containing the macrocycle; hence, two identical ligands are bound to the *trans*-axial coordination sites on ruthenium. The spectrum also displays a pair of doublets located well upfield of tetramethylsilane which are consistent with two coordinated ethylene sulfide molecules and which suggest that the these ligands are stereochemically rigid on the NMR time scale, giving rise to the observed splitting.

Single-crystal X-ray analysis of **1** (Figure 2) reveals what we believe to be the first structurally characterized complex possessing two ethylene sulfide ligands. The structure is entirely consistent with previously published structures of the bis(thio ether) complexes, Ru(OEP)(SRR′)$_2$ (R = R′ = Ph; R = *n*-decyl, R′ = Me).[14] The fact that the two ethylene sulfide ligands are tilted relative to the macrocyclic plane is also consistent with a ruthenium(II) ethylene sulfide complex reported by Rauchfuss et al. which showed that the sulfur atom prefers a pyramidal geometry, giving rise to chemical shift inequivalent pairs of endo and exo protons.[15]

Because ethylene sulfide is known to be a sulfur atom donor,[16] we examined the product of heating a freeze-dried sample of **1** to 130 °C under high vacuum (Figure 1). Freeze-drying was carried out to facilitate the loss of any gaseous products. If **1** had lost two molecules of ethylene, as we expected, the resulting product would have been the unknown symmetric *trans*-disulfide complex, Ru(OEP)(S)$_2$, homologous to known *trans*-dioxo ruthenium(VI) porphyrin complexes mentioned

---

(13) G. M. Sheldrick, SHELXTL, *A Program for Crystal Structure Determination.* Version 5, 1995, Siemens Analytical X-ray Instruments, Madison, WI.

(14) James, B. R.; Pacheco, A.; Rettig, S. J.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 2414.

(15) Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1988**, *110*, 2332.

(16) Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1988**, *110*, 2332 and references therein.

Table 2. Summary of Structural Data for Related Single-Atom-Bridged Compounds

	$[Ru(OEP)]_2S$	$[Fe(OEP)]_2O$ (t)[c]	$[Fe(OEP)]_2O$ (m)[b]
M−Y bond length (Å)[a]	2.12	1.75	1.75
M−Y−M bond angle (deg)	135.7	172.2	176.2
interplanar angle (deg)[d]	24	7.3	2.7
displacement of M (Å)[e]	3.24	3.82	4.47
closest contact (Å)	3.24	3.82	4.47
closest nonbonded atoms	C(12)−C(13A)[f]	C(24)−C(31)	C(24)−C(31)

[a] Y = O or S. [b] Monoclinic unit cell. [c] Triclinic unit cell. [d] Mean planes of 24 core atoms in the macrocycle. [e] From the mean plane of 24 core atoms and toward the bridging atom. [f] C(12) is a *meso* carbon on one ring; C(13A) is an α pyrrolic carbon on the other ring.

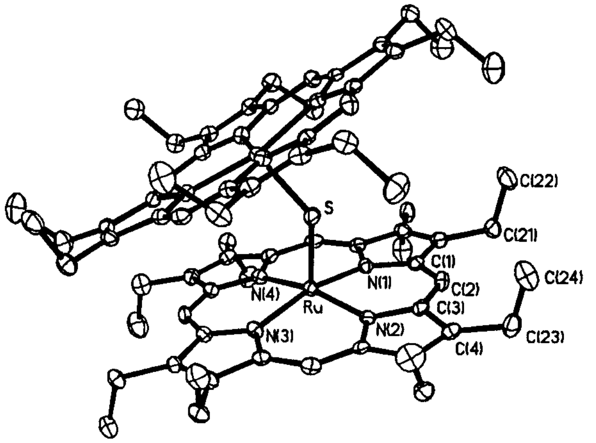

Figure 3. Thermal ellipsoid plot at 50% probability of $[Ru(OEP)]_2S$ (**2**). Hydrogen atoms have been omitted for clarity.

above.[9] However, heating gave a diamagnetic,[17] air-sensitive, purple product (**2**) whose NMR showed loss of the axial ligands. In addition, instead of a simple quartet due to the methylene protons of the peripheral ethyl groups, a pair of multiplets was observed. This suggested that the product now possessed diastereotopic methylene groups, indicative of the loss of the plane of symmetry containing the porphyrin. The degree to which these diastereotopic methylene protons were resolved (two nonoverlapping multiplets) suggested a dimeric structure with one or more bridging sulfur atoms.[18]

Subsequent crystallographic analysis of this compound has shown it to be a sulfur-bridged dimer, (μ-sulfido)bis[(octaethylporphyrinato)ruthenium(III)], $[Ru(OEP)]_2S$ (**2**) (Figure 3). A lone sulfur atom joins the two ruthenium centers, unsupported by any metal−metal bond or other bridging ligand.[19] Previously, this structure was proposed for a series of dinuclear ruthenium(III) nitrosyl complexes, $[Ru(NO)X_2L]_2S$, where L = PPh_3 or $AsPh_3$ and X = Br or Cl; however, these complexes were not structurally characterized.[20]

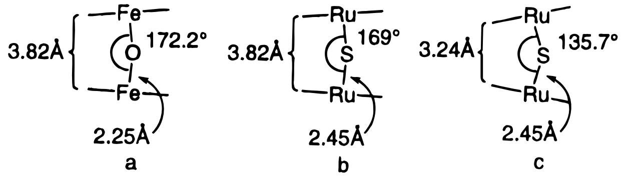

Figure 4. Observed and predicted M−Y-M bond angles. The indicated bond lengths are the sum of the measured bond length and the mean displacement of the metal from the porphyrin core.

The Ru−S−Ru bond angle in **2** is 135.7° (Table 1), and the angle between the mean planes of the two macrocycles is 24°. The closest intramolecular, interplanar atom−atom distance is 3.24 Å between atoms C(12) and C(13A), which is only slightly larger than the sum of the van der Waals radii for two carbon atoms.[21] This distance is comparable to the closest contact distance (3.19 Å) in $[Ru(OEP)]_2$.[22]

To understand why **2** prefers the bent geometry, we first compare it to the recently reported structure of homologous $[Fe(OEP)]_2O$, which exists in two crystal polymorphs, monoclinic and triclinic (Table 2). As expected, the Fe−O−Fe bond angles in $[Fe(OEP)]_2O$ are nearly 180° at 176.2° and 172.2°, respectively. The angle between the mean planes are 2.7° and 7.3°, respectively, indicating nearly parallel macrocycles. The closest intramolecular, interplanar atom−atom distances are 4.47 and 3.82 Å, respectively.

For both the iron and ruthenium complexes, the observed M−Y−M angle is determined by the presence of a minimum in the potential energy curve as a function of bond angle and is a compromise between the electronic preference at Y (oxygen or sulfur) to be bent and the preference for linearity based on minimizing $\pi-\pi$ repulsions. As shown in the calculation by Hoffman, the Fe−O−Fe Walsh diagram indicates only a modest preference for bent geometry; hence the geometry adopted is nearly linear.[4] Similarly, for ruthenium(III) oxo-bridged species such as (μ-oxo)bis[aquabis(2,2′-bipyridine)ruthenium(III)], the observed Ru−O−Ru bond angle is 165.4° which again indicates only mild preference at oxygen for bent geometry.[23]

For **2**, it must be the case that the electronic preference at sulfur for a bent Ru−S−Ru bond is considerably greater than for either of the above two cases because the bent geometry occurs at the expense of greater interplanar repulsions. This may be seen by examining the predicted Ru−S−Ru angle based on simple trigonometry. By considering the effect of the greater M−Y bond length in **2** while restricting the geometry to maintain the minimum interplanar separation observed in the more sterically demanding triclinic $[Fe(OEP)]_2O$ (3.82 Å, Figure 4a), the predicted structure is only slightly more bent (∠Ru−S−Ru = 169°, Figure 4b). However, the observed Ru−S−Ru angle, 135.7°, in **2** is such that two carbon atoms at the periphery

---

(17) The observed chemical shifts are similar to those of diamagnetic [(octaethylporphyrinato)ruthenium(II)] compounds described in ref 11b.

(18) A second possibility (from the elimination of two ethylene molecules and two ethylene sulfide molecules) would have been an analog to the known disulfur-bridged ruthenium pentammine dimer, $[(NH_3)_5RuSSRu(NH_3)_5]X_4 \cdot 2H_2O$, X = Cl, Br. (a) Brulet, C. R.; Iseid, S. S.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 4758−4659. (b) Elder, R. C.; Trkula, M. *Inorg. Chem.* **1977**, *16*, 1048−1051.

(19) A search of the Cambridge Structural Database (Allen, F. H.; Kennard, O. *Chem. Des. Automation News* **1993**, *8*, 1, 31−37) reveals that there is only one remotely related structure involving ruthenium, μ^2-(pentafluorophenylthiolato)pentafluorophenylbis(η^5-pentamethylcyclopentadienyl)diruthenium(III). This molecule possesses, in addition to the Ru−S−Ru moiety, a bridging arylsulfido ligand and a ruthenium metal−metal bond. The resulting Ru−S−Ru bond angle in this compound is 74°. Hornig, A.; Tietmann, C.; Englert, U.; Wagner, T.; Kolle, U. *Chem. Ber.* **1993**, *126*, 2609.

(20) Pandey, K. K. *Spectrochim. Acta* **1983**, *39A* (10), 925−928.

(21) (a) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. (b) Allinger, N. L.; Hirsch, J. A.; Miller, M. A.; Tyminski, I. J.; Van-Catledge, F. A. *J. Am. Chem. Soc.* **1968**, *90*, 1199.

(22) Collman, J. P.; Barnes, C. E.; Swepston, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 3500.

(23) Gilbert, J. A.; Eggleston, D. S.; Murphy, W. R., Jr.; Geselowitz, D. A.; Gersten, S. W.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3855−3864.

of the macrocycle are driven to be essentially in van der Waals contact (Figure 4c). Thus, we conclude that the electronic structure at sulfur is playing a significant role in determining the Ru−S−Ru bond angle.

Valence bond theory appears to offer a simple explanation for the observed structure. It is well-known that the energetic cost of hybridization is higher for sulfur than for oxygen. This is seen in the much smaller H−S−H bond angle in H_2S (92°) as compared to the H−O−H bond angle in water (104.5°).[24] From H_2S, it is apparent that sulfur would prefer to use pure p orbitals to form bonds. Because the hydrogen atoms are so small, there is almost no steric repulsion energy cost to do this; however, the cost is not zero because the observed bond angle would then be strictly 90°.

For $[Fe(OEP)]_2O$, the hybridization at oxygen is nearly sp, but for **2** the hybrid contains more p and less s character (approximately $s^{0.42}p^{0.58}$ based on the observed bond angle).[25] Unlike H_2S, there is a significant steric price to pay in bending, so there is still a large s component to the hybrid. One would assume that the Ru−S−Ru bond would prefer to be more bent; however, any additional bending is offset by the energetic cost of much greater interplanar steric repulsions. (Two peripheral carbon atoms in the structure are already essentially touching.) This assertion is supported by the structurally characterized salen complex, $[Fe(salen)]_2S$,[26] in which the Fe−S−Fe bond angle of 121.8° is much smaller than the corresponding 139° Fe−O−Fe bond angle in $[Fe(salen)]_2O{\cdot}(py)_2$.[5] Again, the sterically less demanding salen ligand allows for a more bent geometry, and sulfur prefers to be bent much more than oxygen.

The observed diamagnetism in $[Ru(OEP)]_2S$, which consists of formal Ru(III) centers, may be rationalized by postulating strong antiferromagnetic coupling between the metals mediated by sulfur. This idea is supported by the fact that corresponding Fe(III) centers in all Fe−O−Fe structures are strongly antiferromagnetically coupled with typical coupling constants, J, of -170 to -230 cm^{-1}.[27] Similarly, sulfur effectively mediates antiferromagnetic coupling as may be seen in $[Fe(salen)]_2S$, which displays a similar J of -172 cm^{-1} (compared to -178 for $[Fe(salen)]_2O$).[26] Alternatively, if the Walsh diagram for Fe−O−Fe described earlier may be considered to be qualitatively valid for Ru−S−Ru, then decreasing of the bond angle from 180° lowers the symmetry which would be expected to split the degeneracy of the HOMO and also lead to a low-spin configuration.[4]

In summary, we have prepared $[Ru(OEP)]_2S$, the closest available homologue in ruthenium porphyrin chemistry to $[Fe(OEP)]_2O$. The complex is diamagnetic and possesses an unsupported sulfur atom bridge. The observed Ru−S−Ru bond angle is 135.7° in contrast to the nearly linear geometry of the iron complex. The closest interplanar contacts for ruthenium are nearly at the van der Waals radius for carbon, indicating a strong electronic preference at sulfur for the bent geometry.

Acknowledgment. The authors thank Drs. Robert Barkley and Katheryn Resing for mass spectral analysis and Professors John McDevitt, James Collman, and Scott Bohle for helpful discussion. This work was partially supported by PRF Grant 27999-G3 and NSF Grant CHE-9505926.

Supporting Information Available: Listings of complete crystal data, components of the anisotropic temperature factors, hydrogen atomic positional and thermal parameters, and bond lengths and angles for $[RuOEP]_2S$ and $Ru(OEP)(SC_2H_4)_2$ (20 pages). Ordering information is given on any current masthead page.

IC961511I

---

(24) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; HarperCollins: New York, 1993; p 226.

(25) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; HarperCollins: New York, 1993; p 222.

(26) Dorfman, J. R.; Girerd, J.-J.; Simhon, E. D.; Stack, T. D. P.; Holm, R. H. *Inorg. Chem.* **1984**, *23*, 4407.

(27) Kahn, O. *Molecular Magnetism;* VCH: New York, 1993; pp 114−115.