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Reactivity of Dioxoosmium(VI) Porphyrins toward Arylhydrazine. Isolation of Hydrazidoosmium and Amidoosmium Porphyrins

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Reactions of dioxoosmium(VI) porphyrins [Os^{VI}(Por)O_2] with excess 1,1-diphenylhydrazine in tetrahydrofuran at ca. 55 °C for 15 min afforded bis(hydrazido(1–))osmium(IV) porphyrins [Os^{IV}(Por)$(NHNPh_2)_2$] (**1a**, Por = TPP (*meso*-tetraphenylporphyrinato dianion); **1b**, Por = TTP (*meso*-tetrakis(*p*-tolyl)porphyrinato dianion)), hydroxo(amido)osmium(IV) porphyrins [Os^{IV}(Por)(NPh_2)(OH)] (**2a**, Por = TPP; **2b**, Por = TTP), and bis(hydrazido(2–))osmium(VI) porphyrin [Os^{VI}(Por)$(NNPh_2)_2$] (**3c**, Por = TMP (*meso*-tetramesitylporphyrinato dianion)). The same reaction under harsher conditions (in refluxing tetrahydrofuran for ca. 1 h) gave a nitridoosmium(VI) porphyrin, [Os^{VI}(Por)(N)(OH)] (**4b**, Por = TTP). Oxidation of **1a**,**b** with bromine in dichloromethane afforded bis(hydrazido(2–)) complexes [Os^{VI}(TPP)$(NNPh_2)_2$] (**3a**) and [Os^{VI}(TTP)$(NNPh_2)_2$] (**3b**), respectively. All the new osmium porphyrins were identified by ^{1}H NMR, IR, and UV–vis spectroscopy and mass spectrometry; the structure of **2b** was determined by X-ray crystallography (Os–NPh_2 = 1.944(6) Å, Os–OH = 1.952(5) Å).

Introduction

Dioxoosmium(VI) porphyrins [Os^{VI}(Por)O_2][1–3] are generally much less reactive than their ruthenium counterparts [Ru^{VI}(Por)O_2].[4,5] While it is reported that [Os^{VI}(Por)O_2] can react with PR_3,[6] "ROH + $SnCl_2$ or ascorbic acid",[2,7,8] RSH,[8,9] and Br_2[8] to afford osmium porphyrins [Os^{II}(Por)$(PR_3)_2$], [Os^{IV}(Por)$(OR)_2$], [Os^{IV}(Por)$(SR)_2$], and [Os^{IV}(Por)Br_2], respectively, the reactivity of [Os^{VI}(Por)O_2] toward N reagents has been rarely studied (a notable exception is the reaction of [Os^{VI}(Por)O_2] with hydrazine hydrate to give dinitrogen complexes [Os^{II}(Por)(N_2)(THF)] in tetrahydrofuran or bis(ammine) complexes [Os^{II}(Por)$(NH_3)_2$] in dichloromethane/methanol[10–13]). This is in contrast with the case of dioxoruthenium(VI) porphyrins [Ru^{VI}(Por)O_2], which have been found to rapidly react with a variety of N reagents such as amines,[14–18,] hydroxylamines,[19] imines,[20] and arylhydrazines.[21]

Our study on the reactivity of [Os^{VI}(Por)O_2] toward an arylhydrazine aims to gain access, through such reactions, to a hydrazidoosmium porphyrin complex, whose synthesis has not been reported in the literature. We envisaged that reaction of [Os^{VI}(Por)O_2] with an arylhydrazine may generate a bis(hydrazido(1−))osmium(IV) porphyrin, parallel to the

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reactions of [$Ru^{VI}(Por)O_2$] with arylhydrazine to form bis(hydrazido(1−))ruthenium(IV) porphyrins.[21] The bis(hydrazido(1−))osmium(IV) porphyrins, if indeed obtainable, could serve as good precursors to bis(hydrazido(2−))osmium(VI) porphyrins. Note that (hydrazido(2−))ruthenium/osmium porphyrins resemble their imido and nitrido analogues as M−N multiply bonded species. Despite the reports of a number of bis(imido)ruthenium(VI)/osmium(VI),[12,14,22] oxo(imido)ruthenium(VI)/osmium(VI),[12,14,18] and nitridoruthenium(VI)/osmium(VI)[13,23] porphyrins, no ruthenium/osmium porphyrins bearing a hydrazido(2−) group are known. Our efforts to oxidize bis(hydrazido(1−))ruthenium(IV) porphyrins to the corresponding bis(hydrazido(2−))ruthenium(VI) species were unsuccessful; however, parallel oxidation for osmium might be less difficult given the substantially higher stability of osmium(VI) porphyrins than their ruthenium(VI) analogues.

Herein we report on the reactions of dioxoosmium(VI) complexes of several tetraarylporphyrins (Por = TPP (**a**), TTP (**b**), TMP (**c**)) with 1,1-diphenylhydrazine, which not only result in isolation of bis(hydrazido(1−))osmium(IV) porphyrins [$Os^{IV}(Por)(NHNPh_2)_2$] (**1a**,**b**), but also give hydroxo(amido)osmium(IV) porphyrins [$Os^{IV}(Por)(NPh_2)(OH)$] (**2a**,**b**), bis(hydrazido(2−))osmium(VI) porphyrin [$Os^{VI}(TMP)(NNPh_2)_2$] (**3c**), and nitridoosmium(VI) porphyrin [$Os^{VI}(TTP)(N)(OH)$] (**4b**), depending on the porphyrinato ligand used and on the reaction conditions. The bis(hydrazido(1−))osmium(IV) porphyrins **1a**,**b** have been successfully converted to bis(hydrazido(2−))osmium(VI) porphyrins [$Os^{VI}(Por)(NNPh_2)_2$] (**3a**,**b**) through bromine oxidation.

Experimental Section

General Procedures. 1,1-Diphenylhydrazine hydrochloride (Aldrich, 97%) and sodium hydroxide pellets (Fisher) were used as received. Tetrahydrofuran (AR, Ajax) was distilled over sodium benzophenone. All other solvents were of AR grade (unless otherwise specified) and used without purification. The complexes [$Os^{VI}(Por)O_2$] (Por = TPP, TTP, TMP) were synthesized according to literature methods.[8] Ultraviolet−visible (UV−vis) spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer (interfaced with an IBM-compatible PC) or a Perkin-Elmer Lambda 19 spectrophotometer. ^1H NMR spectra were recorded on a Bruker DPX 300 spectrometer. Chemical shifts (δ, ppm) are relative to the peak for tetramethylsilane. Infrared (IR) spectra were obtained on a Bio-Rad FT-IR spectrometer. Fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT 95 mass spectrometer using 3-nitrobenzyl alcohol as the matrix. Electrospray mass spectra were measured on a Finnigan LCQ quadrupole ion trap mass spectrometer. Samples were dissolved in HPLC dichloromethane and filtered. The spray and capillary voltages were 4.0 and 22 eV, respectively. Elemental analyses were performed by the Institute of Chemistry, Chinese Academy of Sciences.

Isolation of Bis(hydrazido(1−))osmium(IV) Porphyrins [$Os^{IV}(Por)(NHNPh_2)_2$] (1) and Hydroxo(amido)osmium(IV) Porphyrins [$Os^{IV}(Por)(NPh_2)(OH)$] (2). To a mixture of 1,1-diphenylhydrazine hydrochloride (38 mg, 0.17 mmol) and sodium hydroxide (10 mg, 0.25 mmol) in freshly distilled tetrahydrofuran (10 mL) in the presence of activated molecular sieves (4 Å) was added [$Os^{VI}(Por)O_2$] (Por = TPP or TTP, 0.03 mmol) under argon. The mixture was heated at ca. 55 °C for 15 min to give a red solution. After removal of solvent in vacuo, the oily residue was dissolved in dichloromethane and then filtered. The filtrate was transferred onto an alumina column. Hexane and dichloromethane were sequentially used as eluents to remove any unreacted 1,1-diphenylhydrazine and [$Os^{VI}(Por)O_2$]. The desired products **1** and **2** were eluted with a dichloromethane/chloroform mixture (3:1 v/v) and neat chloroform, respectively.

Data for [$Os^{IV}(TPP)(NHNPh_2)_2$] (1a). Yield: 35%. ^1H NMR (300 MHz, $CDC1_3$): H_β 8.34 (s, 8H), H_o 7.96 (d, 8H), H_m, H_p 7.68 (m, 12H), H'_p 6.67 (t, 4H), H'_m 6.45 (t, 8H), H'_o 3.85 (d, 8H); the NH proton resonances were not located. IR (KBr pellet): 1015 cm^{-1} (oxidation state marker band). UV−vis (1.03×10^{-5} M, CH_2C1_2): λ_{max}/nm (log ϵ) = 408 (4.91), 441 (4.80), 558 (3.99). ESI MS: m/z 1170 $[M]^+$, 818 $[M - NHNPh_2 - NHPh_2]^+$. Anal. Calcd for $C_{68}H_{50}N_8Os$: C, 69.84; H, 4.31; N, 9.58. Found: C, 69.65; H, 4.03; N, 9.52.

Data for [$Os^{IV}(TTP)(NHNPh_2)_2$] (1b). Yield: 37%. ^1H NMR (300 MHz, $CDC1_3$): H_β 8.38 (s, 8H), H_o 7.82 (d, 8H), H_m 7.44 (d, 8H), *p*-Me 2.65 (s, 12H), H'_p 6.57 (t, 4H), H'_m 6.36 (t, 8H), H'_o 3.79 (d, 8H); the NH proton resonances were not located. IR (KBr pellet): 1015 cm^{-1} (oxidation state marker band). UV−vis (9.82×10^{-6} M, CH_2C1_2): λ_{max}/nm (log ϵ) = 406 (4.97), 438 (4.90), 552 (4.13). FAB MS: m/z 1226 $[M]^+$, 874 $[M - NHNPh_2 - NHPh_2]^+$. Anal. Calcd for $C_{72}H_{58}N_8Os$: C, 70.56; H, 4.77; N, 9.14. Found: C, 70.34; H, 4.67; N, 9.10.

Data for [$Os^{IV}(TPP)(NPh_2)(OH)$] (2a). Yield: 43%. ^1H NMR (300 MHz, $CDC1_3$): H_β 7.83 (s, 8H), H_o 8.14 (d, 4H), 7.91 (d, 4H), H_m, H_p 7.83 (m, 12H), H'_m 6.33 (t, 4H), H'_p 6.20 (t, 2H), H'_o 3.49 (d, 4H); the OH proton resonances were not located. IR (KBr pellet): 1010 cm^{-1} (oxidation state marker band). UV−vis (7.09×10^{-6} M, CH_2C1_2): λ_{max}/nm (log ϵ) = 406 (5.12), 492 (4.24). FAB MS: m/z 989 $[M]^+$, 972 $[M - OH]^+$. Anal. Calcd for $C_{56}H_{39}N_5OOs{\cdot}2H_2O$: C, 65.67; H, 4.23; N, 6.84. Found: C, 65.31; H, 4.02; N, 6.65.

Data for [$Os^{IV}(TTP)(NPh_2)(OH)$] (2b). Yield: 48%. ^1H NMR (300 MHz, $CDC1_3$): H_β 7.84 (s, 8H), H_o 8.02 (dd, 4H), 7.81 (dd, 4H), H_m 7.50 (m, 8H), *p*-Me 2.66 (s, 12H), H'_m 6.30 (t, 4H), H'_p 6.16 (t, 2H), H'_o 3.44 (d, 4H); the OH proton resonances were not located. IR (KBr pellet): 1010 cm^{-1} (oxidation state marker band). UV−vis (5.98×10^{-6} M, CH_2C1_2): λ_{max}/nm (log ϵ) = 408 (5.13), 496 (4.29). ESI MS (CH_2C1_2): m/z 1045 $[M]^+$, 1028 $[M - OH]^+$. Anal. Calcd for $C_{60}H_{47}N_5OOs{\cdot}2H_2O$: C, 66.71; H, 4.76; N, 6.48. Found: C, 66.36; H, 4.96; N, 6.62.

Oxidation of Bis(hydrazido(1−))osmium(IV) Porphyrins [$Os^{IV}(Por)(NHNPh_2)_2$] (1) to Bis(hydrazido(2−))osmium(VI) Porphyrins [$Os^{VI}(Por)(NNPh_2)_2$] (3). Complex **1** (0.025 mmol) was dissolved in dichloromethane (5 mL). A dilute solution of bromine (60 mM) in dichloromethane (ca. 5 drops) was added, and the mixture was stirred for 15 min to give a red-green solution. Removal of the solvent by rotary evaporation afforded a dark purple solid.

Data for [$Os^{VI}(TPP)(NNPh_2)_2$] (3a). Yield: 93%. ^1H NMR (300 MHz, $CDCl_3$): H_β 8.78 (s, 8H), H_o 8.07 (d, 4H), 7.97 (d, 4H), H_m, H_p 7.81 (m, 12H), H'_p 6.93 (t, 2H), 6.72 (t, 2H), H'_m 6.63 (t, 4H), 6.51 (t, 4H), H'_o 3.81 (d, 4H), 3.50 (d, 4H). IR (KBr pellet): 1018 cm^{-1} (oxidation state marker band). UV−vis (1.25×10^{-5} M, CH_2Cl_2): λ_{max}/nm (log ϵ) = 406 (4.92), 509 (4.13). ESI MS: m/z 1168 $[M]^+$, 818 $[M - NNPh_2 - NPh_2]^+$.

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Table 1. Crystallographic Data of **2b**

empirical formula	$C_{60}H_{47}N_5OOs$	a, Å	15.836(3)	V, Å^3	5190(2)
cryst syst	monoclinic	b, Å	23.880(5)	Z	4
fw	1044.23	c, Å	14.720(3)	ρ_{calcd}, g cm^{-3}	1.336
space group	$P2_1/c$	α, deg	90.00	2θ range, deg	51.04
		β, deg	111.20(3)	GOF	0.98
		γ, deg	90.00	R1/wR2	0.045/0.13

Data for [Os^{VI}(TTP)(NNPh$_2$)$_2$] (3b). Yield: 95%. ^{1}H NMR (300 MHz, CD_2Cl_2): H$_\beta$ 8.80 (s, 8H), H$_o$ 7.96 (d, 4H), 7.88 (d, 4H), H$_m$ 7.63 (m, 8H), p-Me 2.73 (s, 12H), H$'_p$ 6.93 (t, 2H), 6.72 (t, 2H), H$'_m$ 6.63 (t, 4H), 6.51 (t, 4H), H$'_o$ 3.81 (d, 4H), 3.48 (d, 4H). IR (KBr pellet): 1017 cm^{-1} (oxidation state marker band). UV−vis (1.55 × 10^{-5} M, CH_2Cl_2): λ_{max}/nm (log ϵ) = 409 (4.80), 510 (4.00). ESI MS: m/z 1225 [M]$^+$, 874 [M − NNPh$_2$ − NPh$_2$]$^+$. Anal. Calcd for $C_{72}H_{56}N_8Os$: C, 70.68; H, 4.61; N, 9.16. Found: C, 70.50; H, 4.49; N, 9.12.

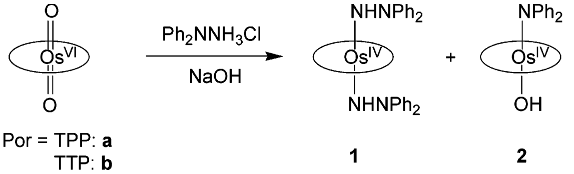
Isolation of Bis(hydrazido(2−))osmium(VI) Porphyrin [Os^{VI}(TMP)(NNPh$_2$)$_2$] (3c). This complex was isolated from the same reaction as for the isolation of **1** and **2**, except that [Os^{VI}(TMP)O$_2$] was used instead of [Os^{VI}(TPP)O$_2$] or [Os^{VI}(TTP)O$_2$]. Chromatography of the reaction mixture on an alumina column with dichloromethane/chloroform (3:1 v/v) as the eluent, followed by removal of the solvents, afforded **3c** as a dark purple solid in 40% yield. ^{1}H NMR (300 MHz, $CDCl_3$): H$_\beta$ 8.71 (s, 8H), H$_m$ 7.33 (s, 4H), 7.21 (s, 4H), p-Me 2.61 (s, 12H), o-Me 1.87 (s, 12H), 1.22 (s, 12H), H$'_p$, H$'_m$ 6.80 (t, 2H), 6.50 (m, 6H), 6.40 (t, 4H), H$'_o$ 3.75 (d, 4H), 3.42 (d, 4H). IR (KBr pellet): 1020 cm^{-1} (oxidation state marker band). UV−vis (2.36 × 10^{-5} M, CH_2Cl_2): λ_{max}/nm (log ϵ) = 409 (4.71), 510 (3.84). ESI MS: m/z 1337 [M]$^+$, 986 [M − NNPh$_2$ − NPh$_2$]$^+$. Anal. Calcd for $C_{80}H_{72}N_8Os$: C, 71.94; H, 5.43; N, 8.39. Found: C, 71.72; H, 5.37; N, 8.15.

Isolation of Nitridoosmium(VI) Porphyrin [Os^{VI}(TTP)(N)(OH)] (4b). This complex was isolated by following the same procedure as for the isolation of complexes **1** and **2** except that (i) the reaction mixture was refluxed for ca. 1 h until it turned green and (ii) after removal of any unreacted 1,1-diphenylhydrazine and [Os^{VI}(TTP)O$_2$] with hexane and dichloromethane, dichloromethane/chloroform (1:3, v/v) was used as the eluent. Yield: 65%. ^{1}H NMR (300 MHz, $CDCl_3$): H$_\beta$ 9.31 (s, 8H), H$_o$ 8.26 (dd, 8H), H$_m$ 7.65 (d, 8H), p-Me 2.77 (s, 3H); the OH proton resonances were not located. IR (KBr pellet): 1018 cm^{-1} (oxidation state marker band). UV−vis (3.05 × 10^{-5} M, CH_2Cl_2): λ_{max}/nm (log ϵ) = 339 (4.47), 389 (4.70), 475 (4.45), 593 (3.95), 634 (3.80). ESI MS: m/z 891 [M]$^+$, 874 [M − OH]$^+$. Anal. Calcd for $C_{48}H_{37}N_5OOs\cdot H_2O$: C, 63.39; H, 4.33; N, 7.71. Found: C, 63.78; H, 4.23; N, 7.41.

X-ray Structural Determinations. Diffraction-quality crystals of **2b** were obtained by slow evaporation of a solution of **2b** in dichloromethane/hexane (1:5 v/ v). A purple crystal of dimensions 0.3 × 0.2 × 0.15 mm in a glass capillary was used for data collection at 28 °C on a MAR diffractometer with a 300 mm image plate detector and graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) using the ω scan mode. Data collection was made with 3° oscillation (60 images) at a 120 mm distance and a 300 s exposure. The images were interpreted and intensities integrated using the program DENZO.[24] The structure was solved by direct methods employing the SHELXS-97 program[25] on a PC. The Os and many non-H atoms were located according to the direct methods. The positions of the other non-H atoms were found after successful refinement by full-matrix least-squares using the program SHELXL-97.[26] All 8980 independent reflections from a total of 25447 reflections participated in the full-matrix least-squares refinement against F^2. These reflections were in the ranges $-18 < h < +18$, $-26 < k < +28$, and $-17 < l < +17$. One crystallographic asymmetric unit consists of one formula unit. In the final stage of least-squares refinement, all non-H atoms were refined anisotropically; H atoms except the one on the O atom were generated by the program SHELXL-97. The positions of the H atoms were calculated on the basis of the riding mode with thermal parameters equal to 1.2 times that of the associated C atom, and participated in the calculation of final R indices. Table 1 shows the crystallographic data of **2b**.

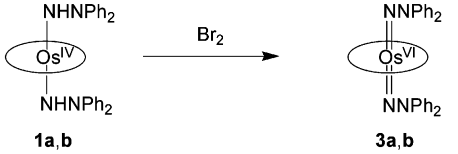
Results

Dioxoosmium(VI) porphyrins [Os^{VI}(Por)O$_2$] were found to rapidly react with an arylhydrazine such as 1,1-diphenylhydrazine at elevated temperature. We first examined such reactions by using the complexes [Os^{VI}(TPP)O$_2$] and [Os^{VI}(TTP)O$_2$], both bearing a simple porphyrinato ligand. When each of the dioxo complexes was treated with excess 1,1-diphenylhydrazine (generated in situ from 1,1-diphenylhydrazine hydrochloride and slightly excess sodium hydroxide) in tetrahydrofuran at ca. 55 °C under argon, the dark green reaction mixture changed, within 15 min, to a red solution containing bis(hydrazido(1−))osmium(IV) porphyrins [Os^{IV}(Por)(NHNPh$_2$)$_2$] (**1a,b**) and hydroxo(amido)osmium(IV) porphyrins [Os^{IV}(Por)(NPh$_2$)(OH)] (**2a,b**) (reaction 1), which were isolated in ca. 35% (**1a,b**) and 45% (**2a,b**) yields upon column chromatography on alumina.



(1)

Treatments of the bis(hydrazido(1−))osmium(IV) porphyrins **1a**,**b** with bromine in dichloromethane at room temperature for 15 min led to the formation of red-green solutions, from which the bis(hydrazido(2−))osmium(VI) porphyrins [Os^{VI}(Por)(NNPh$_2$)$_2$] (**3a**,**b**) were isolated in almost quantitative yield (reaction 2).



(2)

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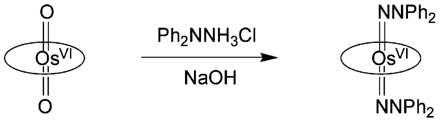
Interestingly, when we extended reaction 1 to [Os^{VI}(TMP)O_2] (which bears a sterically encumbered porphyrinato ligand), the reaction under the same conditions directly afforded bis(hydrazido(2−))osmium(VI) porphyrin [Os^{VI}(TMP)$(NNPh_2)_2$] (**3c**) in 40% yield (reaction 3), together with an unidentified osmium porphyrin in about the same yield. Neither [Os^{IV}(TMP)$(NHNPh_2)_2$] (**1c**) nor [Os^{IV}(Por)(NPh_2)(OH)] (**2c**) was detected.



(3)

Por = TMP: **c**

3c

We have also examined reaction 1 under harsher conditions; that is, the reaction mixture was refluxed for ca. 1 h rather than heated at ca. 55 °C for 15 min. For [Os^{VI}(TTP)O_2], a green solution was obtained, from which the nitridoosmium(VI) porphyrin **4b** was isolated in 65% yield. Under these conditions, no hydrazidoosmium(IV), hydroxo(amido)osmium(IV), or hydrazidoosmium(VI) porphyrins were isolated. A similar phenomenon was observed for [Os^{VI}(TPP)O_2], whose reaction product shows a UV−vis spectrum almost identical with that of **4b** and a mass spectrum with a prominent peak at *m*/*z* 818 assignable to $[Os^{VI}(TTP)(N)]^+$. However, in the case of [Os^{VI}(TMP)O_2], no nitrido complex was detected; the products observed were the same as described above.

Complexes **1a**,**b**, **2a**,**b**, **3a**−**c**, and **4b** are moderately air-stable in the solid state but less stable to moist air in solution. Their mass spectra all exhibit cluster peaks assignable to the corresponding parent ions. For the hydrazido complexes **1a**,**b** and **3a**−**c**, prominent cluster peaks ascribable to the nitrido species $[Os(Por)(N)]^+$ also appear in their mass spectra (MS/MS measurements revealed that such species result from a fragmentation of the parent ions). This resembles the case of [Ru^{IV}(Por)$(NHNPh_2)_2$],[21] whose mass spectra show intense peaks assignable to $[Ru(Por)(N)]^+$. Figure 1 shows the mass spectrum of **3b** as an example, along with the MS/MS spectrum for the corresponding parent ion.

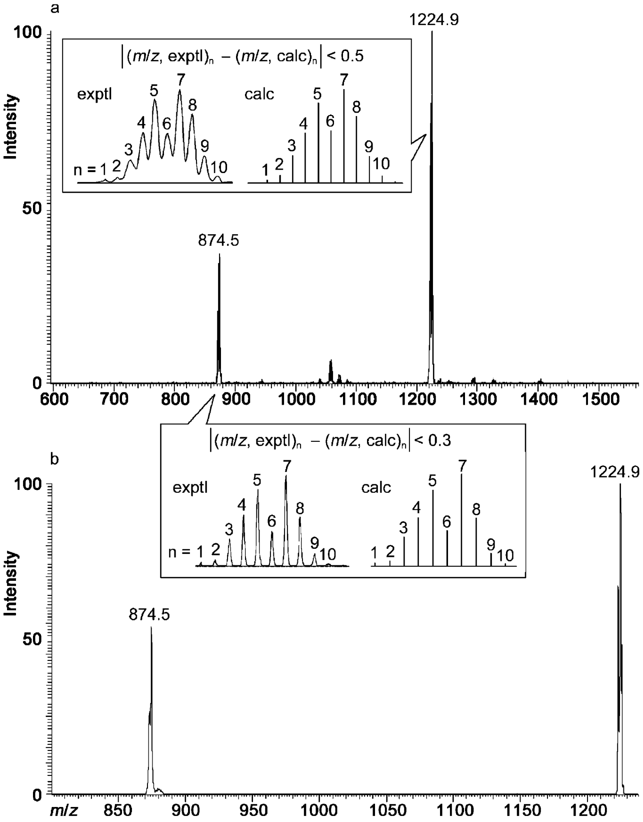


Figure 1. (a) ESI mass spectrum and (b) MS/MS spectrum for the parent ion of **3b**.

The UV−vis spectra of **1a**,**b** appear to show two Soret bands with λ_{max} values of about 407 and 440 nm (note that some previously reported nitrosyl- or nitridoosmium porphyrins also exhibit two Soret bands in their UV−vis spectra[13]). The β bands of **1a**,**b** were located at λ_{max} values of 558 and 552 nm, respectively. Conversion of **1a**,**b** to the complex **3a**,**b** resulted in collapse of the two Soret bands to a single Soret band with a λ_{max} value of about 407 nm, accompanied by a blue shift of the β band to ca. 510 nm. The UV−vis spectrum of **3c** is similar to that of **3a**,**b**. Hydroxo(amido) complexes **2a**,**b** show a Soret band with $\lambda_{max} \approx 406$ nm and a β band with $\lambda_{max} \approx 495$ nm in their UV−vis spectra; the latter is substantially blue-shifted compared with the β bands of **1a**,**b**. The UV−vis spectrum of the nitrido complex **4b** features five well-resolved bands with λ_{max} = 339, 389 (Soret), 475, 593, and 634 nm.

Further identification of **1a**,**b** was facilitated by their ^{1}H NMR spectra, which are almost identical to those of their ruthenium counterparts [Ru^{IV}(TPP)$(NHNPh_2)_2$] and [Ru^{IV}(TTP)$(NHNPh_2)_2$].[21] The ^{1}H NMR spectrum of **4b** with δ = 9.31 (H_β, the pyrrolic protons of the porphyrinato ligand), 8.26 (H_o, the *ortho* protons of the *meso*-phenyl groups), 7.65 (H_m, the *meta* protons of the *meso*-phenyl groups), and 2.77 (Me) is also very similar to that of [Ru^{VI}(TTP)(N)Br] (δ = 9.36 (H_β), 8.23 (H_o), 7.64 (H_m), 2.70 (Me));[23] this nitridoosmium(VI) porphyrin can also be prepared from oxidation of [Os^{II}(TTP)$(NH_3)_2$] with *m*-chloroperoxybenzoic acid, a reaction similar to the oxidation of [Os^{II}(OEP)$(NH_3)_2$] (OEP = octaethylporphyrinato dianion) with peracetic acid in the presence of $HClO_4$ to form [Os^{VI}(OEP)(N)ClO_4] as reported by Buchler and co-workers.[13]

The formulation of **2** as hydroxo(amido)osmium(IV) porphyrins was confirmed by X-ray structure determination of **2b**. Figure 2 shows the ORTEP drawing of the complex with the atom-numbering scheme. Selected bond lengths and angles are given in Table 2. Complex **2b** has an Os−NPh_2 distance of 1.944(6) Å, comparable to the Os−NHPh distances in [TpOs(NHPh)Cl_2] (1.919(6) Å, Tp = hydrotris(1-pyrazolyl)borate) and [TpOs(NHPh)$(CF_3SO_3)_2$] (1.939(8) Å) reported by Mayer and co-workers.[27,28] Such Os−NPh_2 or Os−NHPh distances are similar to the Ru−NHAr distance in [Ru^{IV}(TTP)(NH-*p*-$C_6H_4Cl)_2$] (1.956(7) Å).[18] The Os−OH distance of 1.952(5) Å in **2b** is also similar to the Ru−OH distance of 1.943(5) Å in

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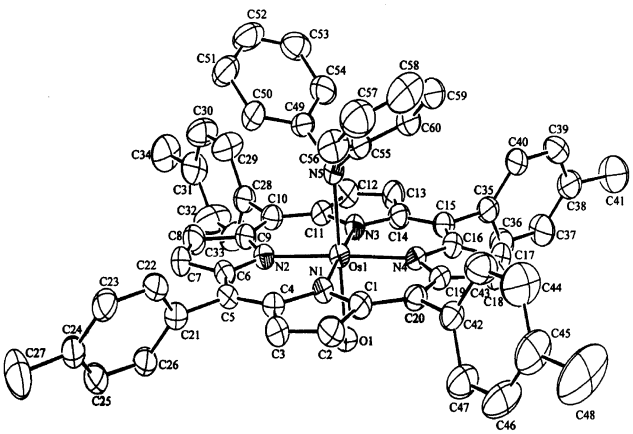

Figure 2. ORTEP drawing of **2b** with atom-numbering scheme.

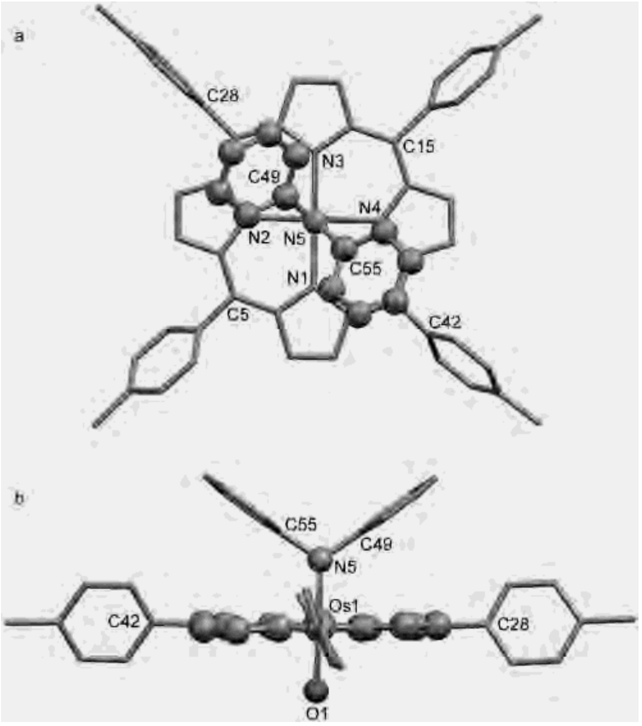

Figure 3. (a) Top view along the N5−O1 axis and (b) side view along the C15−C5 axis of the structure of **2b**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **2b**

Os1−N5	1.944(6)	Os1−O1	1.952(5)
Os1−N1	2.066(6)	Os1−N2	2.085(6)
Os1−N3	2.075(6)	Os1−N4	2.062(6)
N5−C49	1.457(9)	N5−C55	1.454(9)
N5−Os1−O1	177.3(2)	N1−Os1−N3	177.3(2)
N2−Os1−N4	177.5(2)	N1−Os1−N5	90.0(2)
N1−Os1−N4	89.4(2)	N2−Os1−N5	91.2(2)
N2−Os1−N3	89.0(2)	N3−Os1−N4	90.8(2)
N3−Os1−N5	92.7(2)	N1−Os1−N2	90.6(2)
N4−Os1−N5	91.4(2)	N1−Os1−O1	87.3(2)
O1−Os1−N2	89.5(2)	N3−Os1−O1	90.0(2)
O1−Os1−N4	87.9(2)		

[Ru(TTP)(NO)(OH)].[29] As depicted in Figure 3a, the C49, N5, C55 plane of the axial diphenylamido group roughly bisects the N2−Os1−N3 and N1−Os1−N4 angles, with the N2−Os1−N5−C49 torsion angle being about 38.9°. The porphyrin ring is basically planar (Figure 3b), and is almost perpendicular to the axial Os−N and Os−O bonds (N5−Os−O1 angle 177.3(2)°).

Attempts to obtain diffraction-quality crystals of **3a**−**c** have not been successful despite many trials. These osmium(VI) complexes gave typical diamagnetic ^{1}H NMR spectra with H_β signals at $\delta = 8.78$ (**3a**), 8.80 (**3b**), and 8.71 (**3c**), which are substantially downfield from those of the bis(hydrazido(1−))osmium(IV) porphyrins **1a**,**b** ($\delta = 8.34$ and 8.38) but are similar to those of bis(imido)osmium(VI) porphyrins [$Os^{VI}(Por)(NBu^t)_2$] (Por = TPP, TTP; $\delta = 8.72$ and 8.73).[12,14] The oxidation state marker bands of **3a** (1018 cm^{-1}), **3b** (1017 cm^{-1}), and **3c** (1020 cm^{-1}) are also similar to those of [$Os^{VI}(Por)(NBu^t)_2$] (Por = TPP, TTP; 1016 and 1017 cm^{-1}).[12,14]

Discussion

Hydrazidoosmium complexes have previously been isolated only in the presence of non-porphyrin auxiliary ligands. By employing 2,2′:6′,2″-terpyridine or tris(1-pyrazolyl)-methane auxiliary ligand, Meyer and co-workers obtained a number of mononuclear osmium complexes bearing mono-hydrazido(1− or 2−) groups from reactions between the corresponding nitridoosmium complexes and N bases (such as secondary amines) or from electrochemical oxidation of the ammine complexes in the presence of secondary amines.[30−38]

The present reactivity studies of dioxoosmium(VI) porphyrins result in isolation of the first examples of (i) a mononuclear bis(hydrazido)osmium complex and (ii) a hydrazido complex of osmium porphyrin. In general, metalloporphyrins bearing hydrazido axial ligands are sparse. About 20 years ago, Mansuy and co-workers isolated hydrazido(2−)iron(IV) porphyrins [$Fe^{IV}(Por)(NNR_2)$] (NR_2 = 2,2,6,6-tetramethylpiperidin-1-yl).[39,40] Recently, we reported bis(hydrazido(1−))ruthenium(IV) porphyrins [$Ru^{IV}(Por)(NHNPh_2)_2$][21] as mentioned above; Woo and Thorman isolated hydrazido(2−)titanium(IV) porphyrins [$Ti^{IV}(TTP)(NNR_2)$] (R = Me, Ph).[41]

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Although the reactions of dioxoosmium(VI) complexes with excess 1,1-diphenylhydrazine to form [Os^{IV}(Por)($NHNPh_2$)$_2$] (**1a**,**b**) resemble those of their dioxoruthenium(VI) counterparts (which afford [Ru^{IV}(Por)($NHNPh_2$)$_2$] as the main products), the conditions for these [M^{IV}(Por)($NHNPh_2$)$_2$]-formation reactions are quite different. In the case of ruthenium, the [Ru^{IV}(Por)($NHNPh_2$)$_2$] complexes were formed as precipitates simply by stirring suspensions of [Ru^{VI}(Por)O_2] (Por = TPP, TTP) in ethanol containing excess 1,1-diphenylhydrazine at room temperature, and the crude products can be readily purified by recrystallization.[21] However, the reactions between [Os^{VI}(Por)O_2] (Por = TPP, TTP) and 1,1-diphenylhydrazine had to be conducted in homogeneous solution at elevated temperature. Because the reactions also afforded large amounts of hydroxo(amido) complexes **2a**,**b**, purification of the crude **1a**,**b** through recrystallization was difficult.

The formation of nitridoosmium(VI) porphyrins from reactions of [Os^{VI}(Por)O_2] (Por = TPP, TTP) with 1,1-diphenylhydrazine under harsher conditions is interesting. In our previous work, although the mass spectra of [Ru^{IV}(Por)($NHNPh_2$)$_2$] revealed the formation of nitridoruthenium porphyrins in the gas phase under the mass spectroscopic conditions, we were unable to obtain nitridoruthenium porphyrins from the reactions between [Ru^{VI}(Por)O_2] and 1,1-diphenylhydrazine.

Complex **2b** is the sole example of structurally characterized amidoosmium porphyrins, despite the report of several bis(amido)osmium(IV) porphyrins [Os^{IV}(Por)($NHAr$)$_2$].[12] The mononuclear osmium(IV) porphyrins **2a**,**b** each uniquely bind different ligands at the axial sites, in contrast to **1a**,**b**, [Os^{IV}(Por)($NHAr$)$_2$],[12] and other previously reported osmium(IV) porphyrins [Os^{IV}(Por)(X)$_2$] (X = OR,[2,7,8] SR,[8,9] Cl,[7] Br[8]), which invariably bear identical axial ligands.

Since the bis(hydrazido(1−))osmium(IV) porphyrins **1a**,**b** give typical diamagnetic ^{1}H NMR spectra, like [Ru^{IV}(Por)($NHNPh_2$)$_2$],[21] [Os^{IV}(Por)($NHAr$)$_2$],[12] [Ru^{IV}(Por)(NPh_2)$_2$],[15] and [Ru^{IV}(Por)($NHAr$)$_2$],[18] whereas [Os^{IV}(Por)(OR)$_2$],[2,7,8,42] [Os^{IV}(Por)Cl_2],[7] and [Os^{IV}(Por)Br_2][8] give paramagnetic ^{1}H NMR spectra, the ^{1}H NMR spectra of **2a**,**b** that bear amido/hydroxo mixed axial ligands deserve attention. Figure 4a shows the spectrum of **2a** as an example. The splitting of the H_o signals should arise from the lack of an equatorial plane of symmetry in the molecule.

We found that the key spectral features of **2a**,**b** resemble those of previously reported diamagnetic bis(thiolato)osmium(IV) porphyrin [Os^{IV}(TPP)(SPh)$_2$];[8] the major difference lies in their H_o signals (only one H_o signal is observed in [Os^{IV}(TPP)(SPh)$_2$]). Therefore, the hydroxo(amido)osmium(IV) porphyrins **2a**,**b** should also be diamagnetic in nature.

However, comparison of the ^{1}H NMR spectra of **2a**,**b** and [Os^{IV}(TPP)(SPh)$_2$] with those of **1a**,**b**, [Os^{IV}(TPP)($NHPh$)$_2$],[12] and [Ru^{IV}(Por)(NPh_2)$_2$][15] (the spectrum of **1b** is shown in Figure 4b as an example) reveals two unusual features in the spectra of **2a**,**b** and [Os^{IV}(TPP)(SPh)$_2$]. First, the H_β signals (δ = 7.83 for **2a**, 7.84 for **2b**, and 7.79 for [Os^{IV}(TPP)(SPh)$_2$]) are substantially upfield from those of **1a** (δ = 8.34), **1b** (δ = 8.38), [Os^{IV}(TPP)($NHPh$)$_2$] (δ = 8.07), and [Ru^{IV}(Por)(NPh_2)$_2$] (δ = 8.37), and are even upfield from the H_o signals (see Figure 4a). Second, the H'_p signals are upfield from the H'_m signals, opposite the cases of **1a**,**b**, [Os^{IV}(TPP)($NHPh$)$_2$], and [Ru^{IV}(Por)(NPh_2)$_2$] (cf. parts a and b of Figure 4). This is reminiscent of the ^{1}H NMR spectra of paramagnetic osmium(IV) porphyrin [Os^{IV}(TPP)(OCH_2Ph)$_2$] reported earlier,[42] except that [Os^{IV}(TPP)(OCH_2Ph)$_2$] gives much more upfield H_β (δ 4.15) and H'_o (δ 1.77) signals and substantially more downfield H_o signals (δ 9.34). Accordingly, we measured the ^{1}H NMR spectra of **2b** at different temperatures; they are depicted in Figure 5. Within the temperature range of 233−299 K, the H_β, H_m, and H'_o signals are essentially independent of temperature, and the overall shifts ($\Delta\delta$) of the other signals are not larger than 0.12. These results support the diamagnetic nature of **2a**,**b**. It is interesting that, as the temperature decreases from 299 K, the H'_m and H'_p signals become closer to each other and at 233 K almost collapse to a single signal.

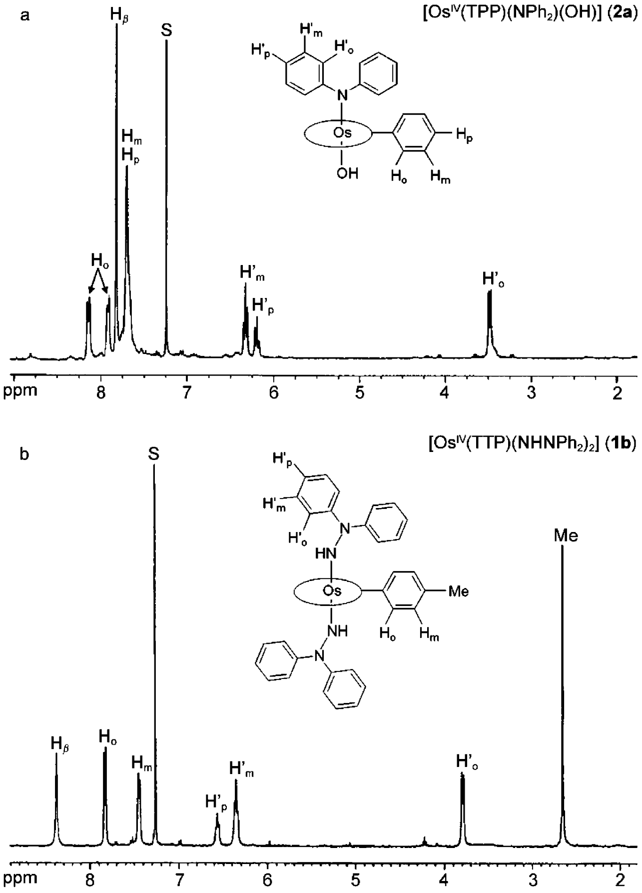

Figure 4. ^{1}H NMR spectra of (a) **2a** and (b) **1b** in $CDCl_3$.

The successful conversions of bis(hydrazido(1−)) complexes **1a**,**b** to bis(hydrazido(2−)) complexes **3a**,**b** through reactions with bromine are not surprising. These reactions apparently occurred via an oxidative deprotonation of **1a**,**b**. Similar oxidative deprotonation reactions with bromine or

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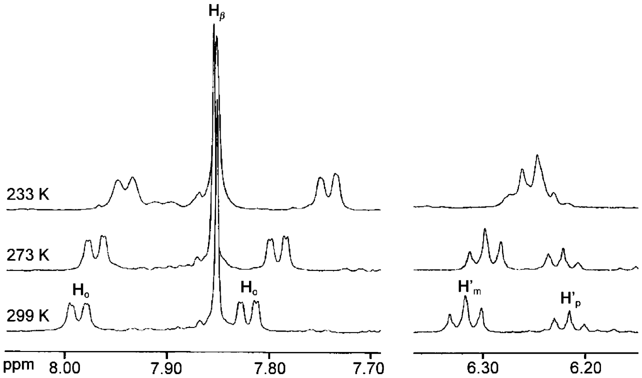

Figure 5. ^{1}H NMR spectra of **2b** in CD_2Cl_2 at different temperatures. The H_m, H'_o, and Me signals are not shown.

air have been applied to prepare bis(amido)ruthenium(IV),[18] bis(imido)osmium(VI),[12,14] or oxo(imido)ruthenium(VI)[12,14] porphyrins in our previous works. We have also observed that reaction of $[Ru^{VI}(TTP)O_2]$ with *tert*-butylamine in refluxing hexane can directly afford a mixture of bis(imido)- and oxo(imido)ruthenium(VI) porphyrins $[Ru^{VI}(TTP)(NBu^t)_2]$ and $[Ru^{VI}(TTP)(O)(NBu^t)]$ (the latter comes from the hydrolysis of the former due to its high moisture sensitivity).[18] The formation of $[Ru^{VI}(TTP)(NBu^t)_2]$ from such reaction formally resembles the direct generation of $[Os^{VI}(TMP)(NNPh_2)_2]$ (**3c**) from the reaction between $[Os^{VI}(TMP)O_2]$ and 1,1-diphenylhydrazine (reaction 3).

A question arises as to why the bis(hydrazido(2−)) complexes **3a**,**b** were not directly isolated from the reactions of $[Os^{VI}(TPP)O_2]$ and $[Os^{VI}(TTP)O_2]$ with excess 1,1-diphenylhydrazine. One possibility is that these reactions could also lead to formation of **3a**,**b**, but both the bis(hydrazido(2−)) complexes degraded to bis(hydrazido(1−)) complexes **1a**,**b** during the reactions (by, for example, reacting with 1,1-diphenylhydrazine). Indeed, treatment of the isolated **3b** with NaOH and $Ph_2NNH_3^+Cl^-$ in tetrahydrofuran under the same conditions as for reaction 1 gave the hydrazido(1−) complex **1b** in ca. 80% isolated yield. This is in contrast with the case of the isolated **3c**, which underwent no appreciable conversion to $[Os^{IV}(TMP)(NHNPh_2)_2]$ (**1c**) upon similar treatment. It might be the case that the bulky and hydrophobic porphyrinato ligand TMP provides a better shield for the $Os{=}NNPh_2$ groups toward attack by external reagents, which significantly retards the degradation of the hydrazido(2−) complex to the hydrazido(1−) complex.

Interestingly, bis(hydrazido(2−)) complexes **3** each give two sets (in a 1:1 intensity ratio) of H_o, H'_p, H'_m, and H'_o signals (see Figure 6 for the spectrum of **3b**), unlike the bis(hydrazido(1−)) complexes **1** (cf. Figures 4b and 6). This suggests that conversion of a bis(hydrazido(1−))osmium(IV) porphyrin to the bis(hydrazido(2−)) counterpart significantly lowers the symmetry of the molecule. Since both the M−N and N−N bonds in the $M{-}N{-}NR_2$ moieties of hydrazido(2−)metal complexes can have multiple bonding characters,[43] possibly such multiple bondings in the $Os{-}N{-}NPh_2$ moieties of **3** render the rotation of the $NNPh_2$ groups about the Os−N bonds and the rotation of the NPh_2 groups about the N−N bonds significantly more difficult. This could make the molecules of **3** lack an equatorial plane of symmetry and cause the two phenyl groups of each $NNPh_2$ axial ligand to be situated in different environments, if the $Os{-}N{-}NPh_2$ moieties are bent (note the bent hydrazido(2−) coordination in $[Os^{IV}(tpy)(bpy)(NNEt_2)](PF_6)_2$ observed by Meyer and co-workers[30]) or considerably distorted from a strictly linear geometry.

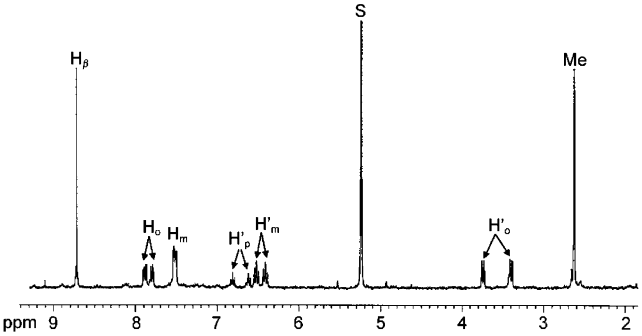

Figure 6. ^{1}H NMR spectrum of **3b** in CD_2Cl_2.

Conclusion

Dioxoosmium(VI) porphyrins readily react with an arylhydrazine such as 1,1-diphenylhydrazine at elevated temperatures. The products in the reactions depend on the types of the porphyrinato ligands employed and on the reaction conditions. By employing TPP and TTP, bis(hydrazido(1−))osmium(IV) and hydroxo(amido)osmium(IV) porphyrins can be isolated in moderate yields; the latter are unique osmium(IV) porphyrins bearing mixed axial ligands. Bromine oxidation of the bis(hydrazido(1−))osmium(IV) porphyrins leads to formation of the corresponding bis(hydrazido(2−))osmium(VI) porphyrins. If a sterically encumbered porphyrinato ligand such as TMP is employed, bis(hydrazido(2−))osmium(VI) porphyrin can be isolated directly from the reaction between dioxoosmium(VI) porphyrin and 1,1-diphenylhydrazine. The present work provides the first access to a mononuclear bis(hydrazido)osmium complex and to a hydrazido complex of osmium porphyrin.

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Supporting Information Available: Positional and thermal parameters and bond lengths and angles for **2b** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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