Reactions of Dimesityldioxoosmium(VI) with Bidentate N-Heterocycles. Crystal Structure of a Dioxoosmium(VI) Complex Containing a Molecular Square

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The interaction of $OsO_2(mes)_2$ (mes = mesityl) with pyz (pyrazine) gave the pyrazine-bridged dimer $[OsO_2(mes)_2]_2(\mu\text{-}pyz)$ (**1**), which has been characterized by X-ray crystallography. The structure around Os in **1** is square pyramidal, with the pyrazine, two oxo ligands, and one mesityl group in the square plane. The Os−O distance and O−Os−O angle are 1.71 Å and 147.5°, respectively. The reaction of $OsO_2(mes)_2$ with 4,4′-bpy (4,4′-bipyridyl) and bpe (*trans*-1,2-bis(4-pyridyl)ethylene) in Et_2O gave the oligomeric $[OsO_2(mes)_2L]_n$ (L = 4,4′-bpy (**2**), bpe (**3**)) in good yields. The ¹H NMR spectra of **2** and **3** indicate that L's are coordinated in a symmetric fashion in these oligomers. The reaction of $OsO_2(mes)_2$ with 4,4′-bpy in $CHCl_3$ followed by slow evaporation afforded the crystalline tetramer $[OsO_2(mes)_2(\mu\text{-}4,4'\text{-}bpy)]_4$ (**4**). The crystal structure of the tetramer **4** contains the square-planar $[Os(4,4'\text{-}bpy)]_4$ core with octahedral local geometry around each Os. The Os−O distance and O−Os−O angle are 1.6 Å and 159°, respectively. Treatment of $OsO_2(mes)_2$ with CNpy (4-cyanopyridine) gave $[OsO_2(mes)_2]\cdot[OsO_2(mes)_2(CNpy)]$ (**5**). The structure of **5** consists of the four-coordinate $[OsO_2(mes)_2]$ and five-coordinate $[OsO_2(mes)_2(CNpy)]$ moieties, which are linked together via the Os=O···Os interaction. The Os−O distances in the $[OsO_2(mes)_2]$ and $[OsO_2(mes)_2(CNpy)]$ moieties in **5** are 1.69 and 1.71 Å, respectively. The (Os)O···Os distance is 2.78 Å, and the Os−O···Os angle is 170°. The Os−O stretching frequency for the above dimesityldioxoosmium(VI) complexes correlates well with the Os−O bond order and the coordination environment around Os.

Introduction

One- and two-dimensional network materials containing transition metals have attracted much attention due to their interesting catalytic, electrical, and optical properties.[1] Of particular interest are "molecular square" materials based on metals and bipyridines, which have been shown to recognize organic molecules and to catalyze reactions.[2] The rich redox chemistry of oxo−osmium complexes[3] coupled with the recent findings

that certain *trans*-dioxo−Os(VI) complexes possess long-lived photoemissive excited states[4] prompted us to synthesize polynuclear and macrocyclic complexes containing the oxo-osmium moiety. Additionally, the $\nu(Os-O)$ value can serve as a probe of the coordination geometry around Os in the oxo−osmium-containing polymers both in solution and in the solid state. Coordinately unsaturated $OsO_2(mes)_2$ (mes = mesityl) has a high affinity for pyridine[5] and, hence, would be expected to be a good building block for polymers of the type $[OsO_2(mes)_2L]_n$ (L = bidentate bridging ligand, e.g. pyrazine, 4,4′-bipyridyl). We herein describe the reactions of $OsO_2(mes)_2$ with bidentate N-heterocycles and the crystal structures of dimeric and macrocyclic complexes containing the $[OsO_2(mes)_2]$ moiety.

Experimental Section

Solvents were purified and distilled prior to use. ¹H NMR spectra (in $CDCl_3$) were recorded on a JEOL EX400 spectrometer. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$. Infrared spectra were recorded on a Perkin-Elmer

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(1) See for example: (a) Hirsch, A.; Hanack, M. In *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics*; Bredas, J. L., Chance, R. R., Eds.; Kluwer: New York, 1990; p 163. (b) Schultz, H.; Lehmann, H.; Rein, M.; Hanack, M. *Struct. Bonding* **1991**, *74*, 41.
(2) (a) Robinson, R.; Abrahams, B. F.; Batten, S. R.; Gable, R. W.; Hoskins, B. F.; Liu, J. In *Supramolecular Architecture*; Bein, T., Ed.; ACS Symposium Series 499; American Chemical Society: Washington, DC, 1992; Chapter 12, and references cited therein. (b) Fujita, M.; Yazaki, J.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. (c) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. (d) Stang, P. J.; Zhdankin, V. V. *J. Am. Chem. Soc.*, **1993**, *115*, 9808. (e) Stang, P. J.; Cao, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 4981. (f) Stang, P. J.; Chen, K. *J. Am. Chem. Soc.* **1995**, *117*, 1667. (g) Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6273. (h) Rauter, H.; Hillgeris, E. C.; Erxleben, A.; Lippert, B. *J. Am. Chem. Soc.* **1994**, *116*, 616.
(3) (a) Che, C.-M.; Yam, V. W.-W. *Adv. Inorg. Chem.* **1992**, *39*, 233. (b) Che, C.-M.; Cheng, W.-K.; Yam, V. W.-W. *J. Chem. Soc., Dalton Trans.* **1990**, 3095. (c) Che, C.-M.; Cheng, W.-K.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1986**, 200. (d) Che, C.-M.; Cheng, W.-K. *J. Am. Chem. Soc.* **1986**, *108*, 4644.

(4) (a) Che, C.-M.; Yam, V. W.-W.; Cho, K.-C.; Gray, H. B. *J. Chem. Soc., Chem. Commun.* **1987**, 948. (b) Yam, V. W.-W.; Che, C.-M. *Coord. Chem. Rev.* **1990**, *97*, 93. (c) Schindler, S.; Castner, E. W., Jr.; Creutz, C.; Sutin, N. *Inorg. Chem.* **1993**, *32*, 4200.
(5) (a) Starvopolous, P.; Edwards, P. G.; Behling, T.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 169. (b) McGrilligan, B. S.; Arnold, J.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1990**, 2465. (c) Chin, K.-F.; Cheng, Y.-K.; Cheung, K.-K.; Guo, C.-X.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1995**, 2967.

Table 1. Summary of Crystal Data and Experimental Details

	1	4	5
formula	$C_{40}H_{46}N_2O_4Os_2$	$[C_{28}H_{30}N_2O_2Os]_4$	$C_{42}H_{48}N_2O_4Os_2$
M_r	999.21	616.76	1025.25
color, habit	blue, block	black, block	black, block
cryst syst	monoclinic	tetragonal	monoclinic
space group	$P2_1/n$ (No. 14)	$I4_1/9$ (No. 88)	$P2_1/n$ (No. 14)
a/Å	9.452(2)	18.318(5)	13.672(2)
b/Å	8.970(4)	18.318(5)	13.539(2)
c/Å	22.451(2)	31.465(6)	21.406(5)
α/deg	90.0	90.0	90.0
β/deg	92.97(1)	90.0	93.01(2)
γ/deg	90.0	90.0	90.0
V/Å^3	1901.0(6)	10 558.3(1)	3957(1)
Z	2	4	4
D_c/g cm^{-3}	1.746	1.552	1.721
$F(000)$	968	4864	1992
diffractometer	Rigaku	Enraf-Nonius	Rigaku
T/K	298	298	298
μ(Mo Kα)/ cm^{-1}	67.14	48.6	64.54
no. of unique rflns	3594	3525	7288
no. of observed rflns ($I > 3.00\sigma(I_0)$)	2530	1962	3991
weighting scheme	$4F_o^2/[\sigma^2(F_o^2) + 0.004(F_o^2)^2]$	$4F_o^2/[\sigma^2(F_o^2) + 0.065F_o^2)^2]$	$4F_o^2/[\sigma^2(F_o^2) + 0.003(F_o^2)^2]$
R^a	0.032	0.040	0.04
$R_w{}^a$	0.035	0.053	0.036
S^b	1.81	1.195	1.85
residual electron density/e Å^{-3}	+0.73 to −0.59	+1.14 to −1.13	+0.95 to −1.01

^{a} $R = \Sigma |F_o| - |F_c|/\Sigma|F_o|$; $R_w = [w (|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. ^{b} $S = [\Sigma\ w(|F_c| - |F_o|)^2/(N_{obs} - N_{param})]^{1/2}$.

16 PC FT-IR spectrophotometer. Elemental analyses were performed by Medac Ltd., Brunel University, U.K.

OsO$_2$(mes)$_2$ was synthesized according to the literature method.[5a] The ligands pyz (pyrazine), 4,4′-bpy (4,4′-bipyridyl), bpe (*trans*-1,2-bis(4-pyridyl)ethylene), and CNpy (4-cyanopyridine) were purchased from Aldrich and used as received.

Synthesis of [OsO$_2$(mes)$_2$]$_2$(μ-pyz) (1). To a solution of OsO$_2$(mes)$_2$ (50 mg, 0.11 mmol) in Et$_2$O (10 mL) was added pyz (9 mg, 0.05 mmol), and the mixture was stirred at room temperature for 1 h. The volatiles were pumped off, and the residue was extracted with hexane/Et$_2$O. Slow evaporation of the extracts afforded dark crystals, which were suitable for a diffraction study (yield 44 mg, 80%). ^{1}H NMR: δ 2.33 (s, 12H, *o*-C*H*$_3$), 2.53 (s, 6H, *p*-C*H*$_3$), 6.99 (s, 4H, *H*$_m$), 8.60 (d, 4H, pyz). IR (Nujol, cm^{-1}): 900 (ν(OsO$_2$)). Anal. Calcd for [C$_{40}$H$_{46}$N$_2$O$_4$Os$_2$]: C, 48.0; H, 4.8; N, 2.8. Found: C, 47.6; H, 5.0; N, 2.5.

Synthesis of [OsO$_2$(mes)$_2$(μ-4,4′-bpy)]$_n$ (2). To a solution of OsO$_2$(mes)$_2$ (50 mg, 0.11 mmol) in Et$_2$O (10 mL) was added a slight excess of 4,4′-bpy (25 mg, 0.16 mmol), and the mixture was stirred for 15 min, during which a copious amount of brown precipitate was formed. The solid was collected, washed with ether, and dried in air (yield 60 mg, 90%). ^{1}H NMR: δ 2.32 (s, 12H, *o*-C*H*$_3$), 2.45 (s, 24H, *p*-C*H*$_3$), 6.94 (s, 4H, *H*$_m$), 7.59 (d, 4H, pyridyl proton), 8.70 (d, 4H, pyridyl proton). Anal. Calcd for [C$_{28}$H$_{30}$N$_2$O$_2$Os]: C, 54.3; H, 5.0; N, 4.8. Found: C, 54.5; H, 4.9; N, 4.5. IR (Nujol, cm^{-1}) 868 ν(OsO$_2$).

Synthesis of [OsO$_2$(mes)$_2$(μ-bpe)]$_n$ (3). This was prepared as for **2** from OsO$_2$(mes)$_2$ (50 mg, 0.11 mmol) and bpe (20 mg, 0.11 mmol) in Et$_2$O (10 mL), isolated as a brown solid (yield 60 mg, 86%). ^{1}H NMR: δ 2.31 (s, 24H, *o*-C*H*$_3$), 2.47 (s, 12H, *p*-C*H*$_3$), 7.26 (s, 2H, C*H*=C), 7.49 (d, 4H, pyridyl proton), 8.54 (d, 4H, pyridyl proton). IR (Nujol, cm^{-1}): 864 (ν(OsO$_2$)), 1610 (ν(C=C)). Anal. Calcd for [C$_{30}$H$_{32}$N$_2$O$_2$Os]: C, 56.1; H, 5.0; N, 4.4. Found: C, 55.7; H, 5.3; N, 4.1.

Synthesis of [OsO$_2$(mes)$_2$(μ-4,4′-bpy)]$_4$ (4). To a solution of OsO$_2$(mes)$_2$ (50 mg, 0.11 mmol) in CHCl$_3$ (10 mL) was added 1 equiv of 4,4′-bpy (18 mg, 0.11 mol) and the solution was left to stand at room temperature for 2 days. Upon slow evaporation, dark green crystals were formed and collected (yield: 34 mg, 50%). ^{1}H NMR: δ 2.32 (s, 12H, *o*-C*H*$_3$), 2.45 (s, 6H, *p*-C*H*$_3$), 6.94 (s, 4H, *H*$_m$), 7.59 (d, 4H, pyridyl proton), 8.70 (d, 4H, pyridyl proton). IR (Nujol, cm^{-1}): 865, 859 (ν(OsO$_2$)). Anal. Calcd for [C$_{28}$H$_{30}$N$_2$O$_2$Os]$_4$: C, 54.3; H, 5.0; N, 4.8. Found: C, 54.5; H, 4.9; N, 4.5.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1

Os(1)−O(1)	1.722(5)	Os(1)−O(2)	1.718(5)
Os(1)−N(1)	2.391(6)	Os(1)−C(3)	2.085(8)
Os(1)−C(12)	2.093(7)		

O(1)−Os(1)−O(2)	147.5(3)	O(1)−Os(1)−N(1)	80.3(3)
O(1)−Os(1)−C(3)	101.0(3)	O(1)−Os(1)−C(12)	96.9(3)
O(2)−Os(1)−N(1)	84.7(3)	O(2)−Os(1)−C(3)	107.2(3)
O(2)−Os(1)−C(12)	93.0(3)	N(1)−Os(1)−C(3)	88.6(3)
N(1)−Os(1)−C(12)	169.9(3)	C(3)−Os(1)−C(12)	101.4(3)

Synthesis of [OsO$_2$(mes)$_2$]·[OsO$_2$(mes)$_2$(CNpy)] (5). To a solution of OsO$_2$(mes)$_2$ (50 mg, 0.11 mmol) in Et$_2$O (10 mL) was added 0.5 equiv of CNpy (6 mg, 0.05 mmol), and the mixture was stirred at room temperature for 30 min. The solvent was pumped off, and the residue was washed with hexane and recrystallized from Et$_2$O/hexane to give dark green crystals (yield: 45 mg, 80%). ^{1}H NMR: δ 2.32 (s, 24H, *o*-CH$_3$), 2.52 (s, 12H, *p*-CH$_3$), 6.98 (s, 8H, H$_m$), 7.62 (d, 2H, pyridyl), 8.76 (d, 2H, pyridyl). IR (Nujol, cm^{-1}): 2239 (ν(C≡N)), 918, 962, 932, 884 (ν(OsO$_2$)). Anal. Calcd for [C$_{42}$H$_{46}$N$_2$O$_4$Os$_2$] : C, 49.3; H, 4.5; N, 2.7. Found: C, 49.0; H, 4.7; N, 2.6.

X-ray Diffraction Meaurements. Data for **1** and **5** were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) and a 12 kW rotating anode generator. Data for **4** were collected on a Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation (λ 0.710 73 Å). The structures for **1** and **4** were solved by direct methods, while the structure for **5** was solved by the Patterson method. These three structures were refined by full-matrix least-squares analyses. All intensity data were corrected for Lorentz and polarization effects. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated in their ideal positions (C−H = 0.95 Å). A summary of crystal data and experimental details is given in Table 1. Selected bond distances and angles for **1**, **4**, and **5** are listed in Tables 2−4, respectively.

Results and Discussion

Syntheses. The interaction of OsO$_2$(mes)$_2$ with 0.5 equiv of pyz (pyrazine) afforded the pyrazine-bridged dimer [OsO$_2$(mes)$_2$]$_2$(μ-pyz) (**1**) in good yield. The solid-state structure of **1** was characterized by X-ray crystal-

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 4

|			
Os−O(1)	1.738(9)	Os−O(2)	1.76(1)
Os−N(1)	2.34(2)	Os−N(2)	2.36(1)
Os−C(1)	2.11(1)	Os−C(10)	2.11(1)
O(1)−Os−O(2)	159.4(4)	O(1)−Os−N(1)	81.5(5)
O(1)−Os−N(2)	83.4(4)	O(1)−Os−C(1)	94.0(6)
O(1)−Os−C(10)	101.2(5)	O(2)−Os−N(1)	83.9(5)
O(2)−Os−C(1)	100.3(5)	O(2)−Os−C(10)	93.2(6)
N(1)−Os−N(2)	87.1(5)	N(1)−Os−C(1)	88.1(5)
N(1)−Os−C(10)	177.0(5)	N(2)−Os−C(1)	174.8(5)
N(2)−Os−C(10)	91.9(5)	C(1)−Os−C(10)	92.9(6)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 5

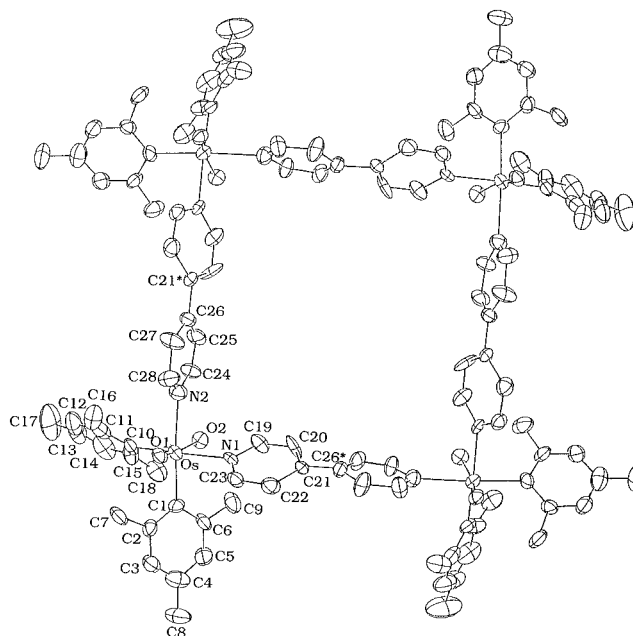|			
Os(1)−O(1)	1.710(7)	Os(1)−O(2)	1.710(8)
Os(1)−N(1)	2.314(8)	Os(1)−C(7)	2.06(1)
Os(1)−C(16)	2.11(1)	Os(2)−O(3)	1.705(7)
Os(2)−O(4)	1.687(7)	Os(2)−C(25)	2.07(1)
Os(2)−C(34)	2.05(1)		
O(1)−Os(1)−O(2)	144.8(3)	O(1)−Os(1)−N(1)	85.2(3)
O(1)−Os(1)−C(16)	92.7(4)	O(1)−Os(1)−C(7)	108.4(4)
O(2)−Os(1)−C(7)	103.5(4)	O(2)−Os(1)−N(1)	81.3 (3)
O(2)−Os(1)−C(16)	97.7(4)	N(1)−Os(1)−C(7)	88.3(3)
N(1)−Os(1)−C(16)	174.7(3)	C(7)−Os(1)−C(16)	96.9(4)
O(3)−Os(2)−O(4)	141.7(4)	O(3)−Os(2)−C(25)	101.5(4)
O(3)−Os(2)−C(34)	96.1(4)	O(4)−Os(2)−C(25)	108.6(4)
O(4)−Os(2)−C(34)	96.1(4)	C(25)−Os(2)−C(34)	97.8(4)

lography and is shown in Figure 1. The geometry around Os in **1** is distorted square pyramidal, with the pyrazine, one mesityl, and two oxo groups in the equatorial plane. The Os−O distance is ca. 1.721 Å, and the O−Os−O angle is 147.5(3)°. The Os−N distance of 2.398 Å is significantly longer than a normal Os^{VI}−N bond (e.g. the Os−N(py) distance in *trans*-OsO₂Cl₂(py)₂ is ca. 2.101 Å[6]), suggesting lability of the coordinated pyrazine. Indeed, the IR spectrum of **1** in CCl₄ shows Os−O stretches due to both OsO₂(mes)₂ (962, 928 cm⁻¹) and **1** (900 cm⁻¹). Upon addition of pyz to a CCl₄ solution of **1**, the 962 and 928 cm⁻¹ bands decrease in intensity and the 900 cm⁻¹ band increases concomitantly. This indicates that **1** is in equilibrium with OsO₂(mes)₂ in solution and the dissociation of pyz in **1** is suppressed by pyz (eq 1).

$$[OsO_2(mes)_2]_2(\mu\text{-pyz}) \rightleftharpoons 2OsO_2(mes)_2 + pyz \quad (1)$$
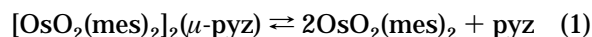
Further addition of pyz led to appearance of a new Os−O band at 874 cm⁻¹, which is typical for an octahedral dimesityldioxoosmium(VI) complex (see below), attributable to the formation of the bis(pyrazine) adduct *trans*-OsO₂(mes)₂(pyz)₂ (eq 2).

$$[OsO_2(mes)_2]_2(\mu\text{-pyz}) + pyz \text{ (excess)} \rightleftharpoons$$
$$2OsO_2(mes)_2(pyz)_2 \quad (2)$$
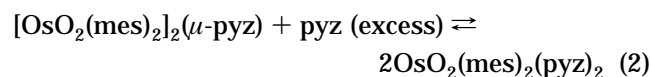
One might expect that the formation of polymers of the type [OsO₂(mes)₂(L)]$_n$ should be favorable for longer spacers L such as 4,4′-bpy (4,4′-bipyridyl) and bpe (*trans*-1,2-bis(4-pyridyl)ethylene). Indeed, the reactions of OsO₂(mes)₂ with and bpe led to isolation of such complexes. However, the nature of the products was found to be dependent on the experimental conditions. Treatment of OsO₂(mes)₂ with 4,4′-bpy and bpe in Et₂O led to immediate precipitation of brown solids analyzed as [OsO₂(mes)₂L]$_n$ (L = 4,4′-bpy (**2**), bpe (**3**)). These

(6) Imbe, Y.; Umakoshi, K.; Matsuanmid, C.; Sasaki, Y. *Inorg. Chem.* **1995**, *34*, 813.
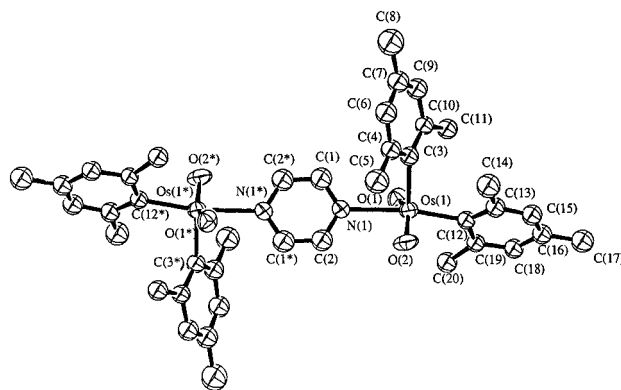
Figure 1. Perspective view of 1 (50% probability ellipsoids).

Figure 2. Perspective view of 4 (50% probability ellipsoids).

materials are insoluble in toluene, acetone, and hexane and slightly soluble in THF and CHCl₃. The value of *n* for **2** in THF solution was determined to be ca. 5 by gel permeation chromatography. The ¹H NMR spectra of **2** and **3** in CDCl₃ show two doublets for the pyridyl protons, suggesting that the L's are bridging ligands and are coordinated symmetrically between two Os centers. The IR spectra of **2** in both Nujol and CCl₄ solution display Os−O stretches at ca. 868 cm⁻¹, indicative of a trans disposition of the two oxo ligands.

On the other hand, the reaction of OsO₂(mes)₂ with 4,4′-bpy in CHCl₃ followed by slow evaporation led to the isolation of the crystalline cyclic tetramer *trans*-[OsO₂(mes)₂(μ-4,4′-bpy)]₄ (**4**), which has been characterized by X-ray crystallography. To our knowledge, **4** represents the first structurally characterized neutral "molecular square" containing a high-valent organometallic building block. Figure 2 shows a perspective view of the molecule. The structure consists of the planar Os₄-(4,4′-bpy)₄ moiety with Os and 4,4′-bpy at each corner and side, respectively. Similar square network structures have been reported for the related cationic materials [M(4,4′-bpy)₂]X (M = Zn, Cd, Cu; X = PF₆, SiF₆),[2c] {[Cd(4,4′-bpy)](NO₃)}∞,[2d] and [Pt(dppp)(4,4′-bpy)]₄(O₃-SCF₃)₈ (dppp = 1,3-bis(diphenylphosphino)propane).[2g]
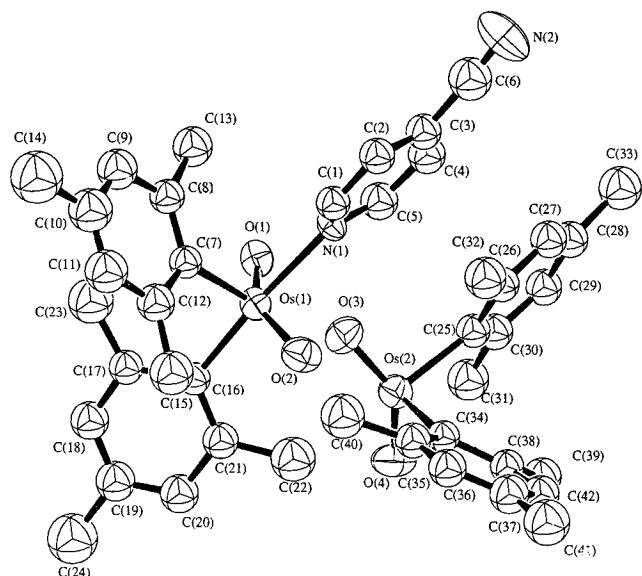
Figure 3. Perspective view of **5** (50% probability ellipsoids).

The local geometry around each osmium is pseudo octahedral with the two 4,4′-bpy and two mesityl groups occupying the equatorial plane; the Os−O distance and O−Os−O angle are ca. 1.75 Å and 159.4°, respectively. The IR spectrum of **4** in Nujol shows intense Os−O stretches at 865 and 859 cm^{-1}. There are two stretching modes for the *trans*-OsO$_2$ entity, possibly due to the bending of O−Os−O. Consistent with the solid-state structure, the ^{1}H NMR spectrum of **4** displays two doublets for the pyridyl protons, indicative of the symmetric binding mode of 4,4′-bpy.

In an attempt to prepare the cyanopyridine-bridged oligomer of OsO$_2$(mes)$_2$, the reaction of OsO$_2$(mes)$_2$ with CNpy (4-cyanopyridine) has also been investigated. Interaction of OsO$_2$(mes)$_2$ with 0.5 equiv of CNpy in Et$_2$O, followed by recrystallization from hexane/Et$_2$O, led to the isolation of [OsO$_2$(mes)$_2$]·[OsO$_2$(mes)$_2$(CNpy)] (**5**). No polymeric materials were obtained, even when a stoichiometric amount of CNpy was used. The structure of **5**, shown in Figure 3, consists of a four-coordinate [OsO$_2$(mes)$_2$] and a five-coordinate [OsO$_2$(mes)$_2$(CNpy)] moiety, which are linked together via the weak Os=O···Os′ interaction. The geometry of the [OsO$_2$(mes)$_2$] moiety is pseudotetrahedral, with an Os−O distance (1.69 Å) similar to that found for OsO$_2$(mes)$_2$.^{5a} The geometry around Os in the [OsO$_2$(mes)$_2$(CNpy)] moiety is approximately trigonal bipyramidal with the two oxo ligands and one mesityl group in the trigonal plane.
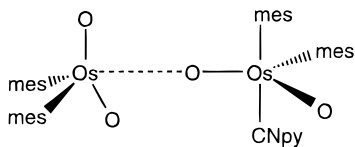

There is no significant difference between the two Os−O distances (ca. 1.71 Å) in the [OsO$_2$(mes)$_2$(CNpy)] moiety, which are similar to those for **1**. The Os=O···Os′ angle is ca. 170°, and the (Os)O···Os′ distance (ca. 2.78 Å) is considerably longer than a normal Os^{VI}−O single bond. The O···Os interaction is weak but significant, at least in the solid state, and can be considered as a donor−acceptor type. The IR spectrum of **5** shows intense

Os−O vibrational modes assignable to both the [OsO$_2$-(mes)$_2$] (918, 932 cm^{-1}) and the [OsO$_2$(mes)$_2$(CNpy)] (884 cm^{-1}) entities.

Bonding and Structure. The structures of OsO$_2$-(mes)$_2$ and its mono and bis adducts are tetrahedral (**I**), square pyramidal (**II**), and octahedral (**III**), respectively.
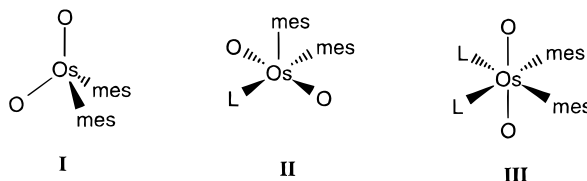
These geometries are in agreement with those predicted by group theory for d^2 dioxometal complexes. Accordingly, the formal Os−O bond orders for **I−III** are 3, 2.5, and 2, respectively.^{7} The Os−N bonds in the adducts **1**, **4**, and **5** are considerably weaker and longer than a normal Os−pyridine bond, obviously due to the strong trans influence of the mesityl ligands. Coordination of bases to OsO$_2$(mes)$_2$ results in a lowering of the Os−O bond order and an increase in steric congestion around Os. This explains why these adducts are unstable in solution with respect to ligand dissociation. It might also be noted that the O−Os−O angle (ca. 150°) in the monoadduct **II** is significantly smaller than the ideal value of 180°. The bending of O−Os−O in **II** can be explained in terms of the maximization of overlap of the filled p$_\pi$(O) orbital with the vacant d$_\pi$(Os) orbital (of b$_2$ symmetry), which is below the equatorial plane.^{7}
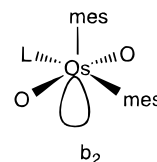
Similar bond angles have been found for the related five-coordinate dioxoosmium(VI) complex [OsO$_2$(mes)-(ONO$_2$)$_2$]$^-$ (O−Os−O angle 146.7(2)°)^{5b} and bis(imido)-osmium(VI) complex Os(NAr)$_2$(PMe$_2$Ph)I$_2$ (Ar = 2,6-diisopropylphenyl, N−Os−N angle 150°).^{8} For the above dimesityldioxoosmium(VI) complexes, the ν(Os−O) value correlates well with the geometry around Os, the Os−O bond length, and the O−Os−O angle, which are collected in Table 5. For example, the ν(Os−O) value varies from 950 cm^{-1} for tetrahedral to 890 cm^{-1} for square pyramidal and to 859 cm^{-1} for octahedral geometry. The Os−O bond length is, however, less sensitive to the change in Os−O bond order and decreases from 1.695 Å or an Os−O double bond to 1.749 Å for an Os−O triple bond.

In summary, we have demonstrated that OsO$_2$(mes)$_2$ reacts with N-bases to give dimeric, tetrameric, and polymeric complexes, depending on the experimental conditions. The Os−O stretching frequency provides valuable information on the solution structure and the coordination environment around Os for these complexes. The study of their photophysical, catalytic, and clathration properties is underway.

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Table 5. Structural and Vibrational Data for the Dimesityldioxoosmium(VI) Complexes

geometry	complex	Os−O (Å)	O−Os−Os (deg)	ν(Os−O) (cm^{-1})
tetrahedral	Os(mes)₂O₂[a]	1.695	136.1	950, 918
	[OsO₂(mes)₂] of **5**	1.69	141.7	932, 918
square pyramidal	**1**	1.710	144.8	900
	[OsO₂(mes)₂(CNpy)] of **5**	1.71	144.8	884
	[OsO₂(mes)(ONO₂)₂]⁻ [b]	1.714	146.7	899
octahedral	**4**	1.749	159.4	865, 859
	OsO₂(mes)₂(tmeda)[c]	1.732	162.7	878
	OsO₂(mes)₂(phen)[c]	1.72	158.5	870

[a] Reference 5a. [b] Reference 5b. [c] Reference 5c. Abbreviations: tmeda = *N,N,N,N*-tetramethylethylenediamine; phen = 1,10-phenanthroline.

Supporting Information Available: Listings of calculated atomic coordinates, bond distances and angles, and anisotropic thermal parameters for compounds **1**, **4**, and **5** (32 pages). Ordering information is given on any current masthead page.

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