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Synthesis and Characterization of an Osmium Porphyrinato Bis(arylimido) Complex, Os(TTP)(NAr)$_2$, with Strongly Bent Osmium–Organoimido Bonds

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Transition metal imido, L_nM–NH, and organoimido, L_nM–NR, complexes are used as models for industrial processes[1] and as reagents for the stereospecific oxyamination[2] and diamination[3] of olefins. We are interested in exploring transition metal imido and organoimido porphyrin[4] complexes since these complexes serve as models for metabolic processes[5] and have been implicated as catalysts for olefin aziridination.[6,7] In addition, the imido ligand has been postulated as a possible intermediate in the nitrite reductase cycle,[8] a metalloenzyme possessing a siroheme[9] active site which can be considered a porphyrin analog. To date, no imido metalloporphyrin complexes have been isolated and only a small number of organoimido metalloporphyrins have been characterized.[6,10–12] Herein we describe the synthesis and characterization of a stable bis(arylimido)osmium(VI) porphyrin complex from the reaction of *p*-nitrophenyl azide with a reactive osmium porphyrin dimer, [Os(TTP)]$_2$.[13] In addition, the results of the first X-ray crystallographic study of an organoimido metalloporphyrin complex are reported.

Experimental Section

^{1}H NMR spectra were obtained with a General Electric QE Plus 300-MHz spectrometer. Visible spectra were run on a Hewlett-Packard 8452A diode array spectrophotometer and infrared spectra on a Perkin-Elmer 1600 Series FTIR. Argon was purified by passing it successively through an Oxiclear gas purifier (Aldrich) and a Drierite gas-drying tube (Fisher). Benzene and hexane were freshly distilled from sodium. Acetonitrile was stirred with CaH$_2$ and distilled from P$_2$O$_5$. All other solvents were reagent grade and were used without further purification. A 450-W medium-pressure Hanovia mercury lamp with a Pyrex shield and a water-cooling jacket was used for photolysis. Os(TTP)(CO)(CH$_3$CN) was prepared according to a literature procedure.[14] The crude product contained metal chlorin impurities which were oxidized using a method first described by Rousseau and Dolphin[15] and modified by Collman et al.[13] *p*-Nitrophenyl azide was prepared according to a literature procedure.[16]

Table 1. Crystallographic Data for Os(TTP)(*p*-NC$_6$H$_4$NO$_2$)$_2$·ether

empirical formula	OsO$_4$N$_8$C$_{60}$H$_{44}$·C$_4$H$_{10}$O
a, Å	10.578(9)
b, Å	15.26(1)
c, Å	18.52(2)
α, deg	99.82(5)
β, deg	98.12(5)
γ, deg	103.80(5)
V, Å^3	2808
crystal shape	prism
Z, molecules/cell	2
crystal class	triclinic
mol wt	1177.37
space group (No.)	$P\bar{1}$ (2)
T, °C	20
wavelength, Å	0.710 73
d_{calcd}, g/cm^3	1.39
linear abs coeff, cm^{-1}	23.3
R(*F*)	0.039
$R_w(F)$	0.046
transm range	0.61–1.00
data collected	four octants
no. of reflns obsd	9817
no. of reflns retained	7945
rejection criterion	$I < 3\sigma(I)$

Synthesis of Os(TTP)(*p*-NC$_6$H$_4$NO$_2$)$_2$. Os(TTP)(CO)(CH$_3$CN) (75 mg, 0.081 mmol) was photolyzed in 30% benzene in CH$_3$CN (300 mL) in a 500-mL three-necked round-bottomed flask equipped with a condenser while argon was bubbled through the solution. Photolysis was continued until the starting material's absorption at 518 nm had disappeared and had been replaced with an absorption at 496 nm indicative of Os(TTP)(CH$_3$CN)$_2$. The solvent was removed under vacuum, and the resulting solid was dissolved in benzene (10 mL). The benzene solution was transferred to a Schlenk tube under argon and frozen in a liquid nitrogen bath. The benzene was removed by sublimation under reduced pressure. The remaining amorphous brick-red solid was heated for 2 h in a 290 °C sand bath at 2×10^{-5} Torr to yield [Os(TTP)]$_2$.[13] *p*-Nitrophenyl azide (29.1 mg, 0.177 mmol) dissolved in benzene (25 mL) was then added to the solid under argon. Immediate gas evolution was observed. The green-brown solution was stirred at room temperature overnight and then loaded onto an alumina column under argon. The column was eluted with 30% benzene in hexane (300 mL) to elute any unreacted *p*-nitrophenyl azide. The solvent was changed to pure benzene to elute a dark green band containing Os(TTP)(*p*-NC$_6$H$_4$NO$_2$)$_2$ (38 mg, 0.034 mmol) in 42% yield. Crystals of Os(TTP)(*p*-NC$_6$H$_4$NO$_2$)$_2$ suitable for elemental analysis and X-ray structure determination were obtained by recrystallization from anhydrous diethyl ether–hexane under argon. UV/vis spectrum in benzene (log ϵ): 406 (5.3), 426 sh (5.2), 500 (4.4), 576 (4.4), 622 nm (4.3). NMR spectrum in CD$_2$Cl$_2$: 8.94 (s, 8 H), 8.02 (d, 8 H, 7.8 Hz), 7.60 (d, 8 H, 7.8 Hz), 6.65 (d, 4 H, 9.2 Hz), 2.72 (s, 12 H), 2.37 ppm (d, 4 H, 9.2 Hz). IR spectrum as KBr pellet: new absorptions present at 1294, 1017, and 924 cm^{-1}.

Crystallographic Details. A summary of crystal data is given in Table 1. The unit cell was determined on a diffractometer using Mo Kα radiation. The lack of diffraction symmetry and systematic extinctions indicated triclinic $P1$ and $P\bar{1}$ as the choices for the space group. Successful refinement in the centrosymmetric $P\bar{1}$ proved this to be the correct space group. An approximately $0.12 \times 0.32 \times 0.35$ mm crystal was mounted in a low-absorption glass capillary for data collection on a CAD4 diffractometer using a 2.0° θ–2θ scan with monochromated graphite Mo Kα radiation. Cell dimensions were determined by least-squares refinement of 25 reflections in the range $25 < 2\theta < 40°$. One standard reflection (236) was monitored every 5000 s and showed no systematic variation. ψ-scan absorption corrections were made. The structure was

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(4) Abbreviations used: TTP = dianion of 5,10,15,20-tetra-(*p*-tolylporphyrin; TPP = dianion of 5,10,15,20-tetraphenylporphyrin.

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Table 2. Fractional Coordinates and Isotropic Thermal Parameters of Selected Atoms in the Os(TTP)(p-$NC_6H_4NO_2$)$_2$ Molecule

atom	x	y	z	B, Å^2
Os	0.11277(2)	0.17257(1)	0.20333(1)	3.376(4)
N1	0.2274(4)	0.2451(3)	0.1396(2)	3.54(9)
N2	0.1237(4)	0.0512(3)	0.1419(2)	3.56(9)
N3	0.0036(4)	0.1009(3)	0.2682(2)	3.8(1)
N4	0.0973(4)	0.2959(3)	0.2651(2)	3.8(1)
N5	−0.0305(4)	0.1815(3)	0.1406(2)	3.8(1)
N7	0.2690(4)	0.1958(3)	0.2682(3)	4.1(1)
C1	0.2730(5)	0.2076(3)	0.0792(3)	3.7(1)
C2	0.2540(4)	0.1132(3)	0.0516(3)	3.6(1)
C3	0.1828(4)	0.0410(3)	0.0803(3)	3.4(1)
C4	0.1666(5)	−0.0554(4)	0.0536(3)	4.3(1)
C5	0.1013(5)	−0.1015(3)	0.0976(3)	4.3(1)
C6	0.0739(5)	−0.0352(3)	0.1541(3)	3.7(1)
C30	0.3171(4)	0.0853(3)	−0.0140(3)	3.5(1)
C70	−0.0885(5)	0.2410(3)	0.1098(3)	3.8(1)
C80	0.3767(5)	0.2657(3)	0.3050(3)	3.9(1)

solved with direct methods using SHELXTL/PC.[17] The non-hydrogen atoms were refined anisotropically. Non-methyl H atom positions were calculated and refined with isotropic temperature factors held fixed and methyl and ether hydrogens not included to $R = 0.039$ and $R_w = 0.046$ using $w^{-1} = \sigma^2(F_o) + 0.0004|F_o|^2$, $\sum w(|F_o| - |F_c|)^2$ minimized. All data reduction, absorption corrections, and refinement were executed using MolEN[18] on a VAX 6510 computer. Scattering factors were those built into MolEN. Graphics were done using MolEN and SHELXTL/PC.

Results and Discussion

Os(TTP)(p-$NC_6H_4NO_2$)$_2$ was prepared in modest yield from the reaction of p-nitrophenyl azide with [Os(TTP)]$_2$. The new porphyrin complex was characterized by ^{1}H NMR, UV/vis, and IR spectroscopy. The ^{1}H NMR spectrum consisted of sharp peaks with the positions of the porphyrin resonances indicative of a diamagnetic osmium center.[19] The aromatic tolyl protons appeared as doublets, which implied symmetric substitution in the axial positions, and the peak integration verified two arylimido ligands per porphyrin ligand. The arylimido protons were shifted upfield compared to those of p-nitrophenyl azide, consistent with their location within the ring current above and below the porphyrin ring. The pyrrole hydrogens of the new porphyrin complex had a somewhat lower chemical shift (8.94 ppm) than the pyrrole hydrogens of the closely related dioxo complex Os(TTP)O_2 (9.16 ppm),[19] which suggests that arylimido ligands are stronger π-donors than oxo ligands.[20]

The UV/vis spectrum of Os(TTP)(p-$NC_6H_4NO_2$)$_2$ was a hyper type similar to that of Os(TTP)(O)$_2$.[19,20] In the IR spectrum, the oxidation marker appeared at 1017 cm^{-1}, consistent with an osmium(VI) formulation.[10b] The new absorptions at 1294 and 924 cm^{-1} were attributed to the arylimido C—N and Os═N stretches, respectively. The energy of the Os═N stretch is higher than that of the Os═O stretch in Os(TTP)O_2 (843 cm^{-1}),[19] which supports the ^{1}H NMR data suggesting that arylimido ligands are stronger π-donors.[20]

The new porphyrin complex was also characterized by X-ray crystallography. A summary of crystal data is given in Table 1. Final values of refined atomic coordinates for significant atoms is given in Table 2, and selected bond lengths and bond angles are presented in Table 3.

A drawing of the porphyrin part of the Os(TTP)(p-$NC_6H_4NO_2$)$_2$ molecule, showing thermal ellipsoids, is shown in Figure 1. The observed bond lengths and angles for the porphyrin skeleton are normal when compared to those of other structurally characterized osmium porphyrins.[19b,21–23] The osmium lies within the porphyrinato plane and is in a distorted octahedral environment. The average Os–N bond distance, 2.062 Å, is normal for an osmium(VI) porphyrin.[19b,21] The porphyrin ring is slightly bent with deviations from the least-squares plane ranging from 0.01 to 0.15 Å. Tolyl rings C30–C36 and C50–C56 are tilted in the same direction with dihedral angles to the porphyrin plane of 120 and 123°, respectively. Tolyl rings C40–C46 and C60–C66 are tilted in opposite directions from each other with dihedral angles of 101 and 77°, respectively, to the plane of the porphyrin. This geometry is similar to that found for Os(TPP)(PPh$_3$)$_2$.[23]

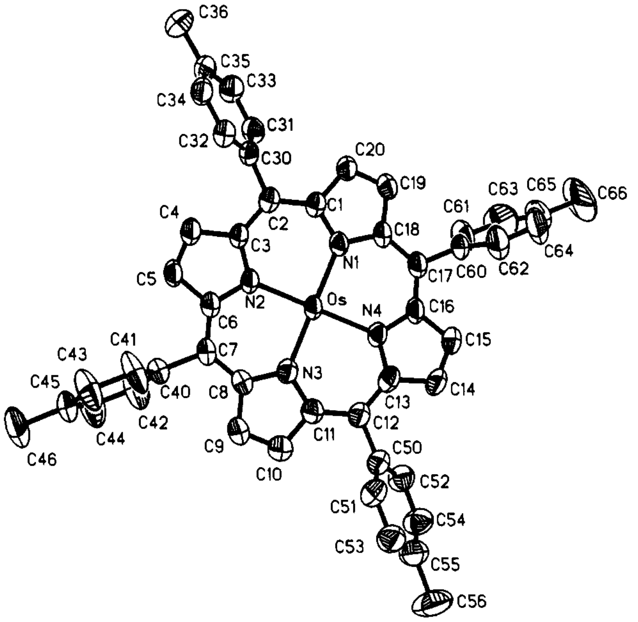

Figure 1. ORTEP drawing for the porphyrin part of the Os(TTP)(p-$NC_6H_4NO_2$)$_2$ molecule showing the atom-numbering scheme. H atoms have been omitted.

Table 3. Selected Bond Distances (Å) and Angles (deg) for the Os(TTP)(p-$NC_6H_4NO_2$)$_2$ Molecule

	Bond Distances		
Os–N1	2.073(4)	C1–C2	1.400(7)
Os–N2	2.039(4)	C2–C3	1.407(7)
Os–N3	2.053(4)	C2–C30	1.514(8)
Os–N4	2.083(4)	C3–C4	1.431(7)
Os–N5	1.822(4)	C4–C5	1.326(8)
Os–N7	1.820(4)	C5–C6	1.438(8)
N1–C1	1.369(7)	N5–C70	1.367(7)
N2–C3	1.380(7)	N7–C80	1.361(6)
	Bond Angles		
Os–N5–C70	144.8(3)	C1–C2–C30	117.8(5)
Os–N7–C80	142.0(4)	N2–C3–C2	125.9(4)
N5–Os–N7	165.1(2)	C3–N2–C6	107.3(4)
N1–Os–N2	90.1(2)	N2–C3–C4	108.1(4)
C1–C2–C3	125.7(5)	C3–C4–C5	108.3(5)

Os(TTP)(p-$NC_6H_4NO_2$)$_2$ is the first structurally characterized porphyrinato organoimido complex and the first example of an octahedral osmium possessing *trans* organoimido ligands. The observed osmium organoimido bond distances (Os–N5 = 1.822(4) Å and Os–N7 = 1.820(4) Å) are significantly shorter than normal Os–N single bonds, which are typically >2.0 Å, but are longer than other structurally characterized osmium organoimido bonds.[24–26] For example, in Os(NBut)O(O_2CBut)$_2$(NH_2But)$_2$,[25] where the osmium similarly is octahedral, is hexavalent, and

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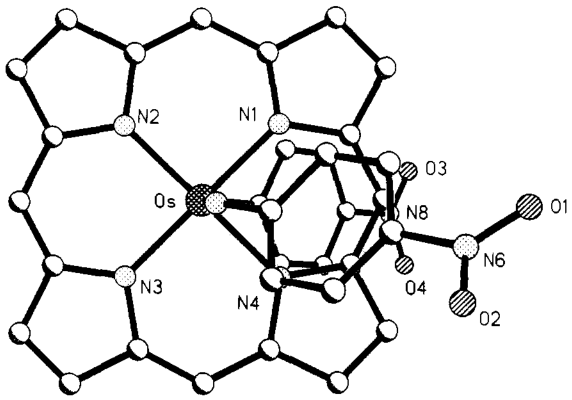

Figure 2. Ball and stick drawing showing the orientation of the arylimido ligands with respect to the porphyrinato plane.

possesses two strong *trans* π-bonding ligands, the metal–organoimido bond length is 1.749(7) Å. In *trans*-Os(NAr)$_2$(PMe$_2$Ph)$_2$ (Ar = 2,6-C$_6$H$_3$-*i*-Pr$_2$),[26] the only other structurally characterized *trans* bis(organoimido)osmium complex, the osmium is square planar and the Os–N bond lengths are 1.790(6) Å.

The orientation of the arylimido ligands with respect to each other and to the porphyrinato plane is shown in Figures 2 and 3. The two axial ligands are nearly coplanar with a dihedral angle of 2.7° between the planes containing Os, N5, C70 and Os, N7, C80. Since a dihedral angle of 90° is expected for two *trans* π-bonding ligands, the observed orientation may be a result of packing forces. The projection of the Os, N5, C70 and Os, N7, C80 planes onto the porphyrinato core make angles of 37.5 and 40.1° with the closest osmium–porphyrin bond, Os–N4. This staggered orientation minimizes axial ligand–porphyrin interaction and allows for maximum axial ligand–metal interaction.[27]

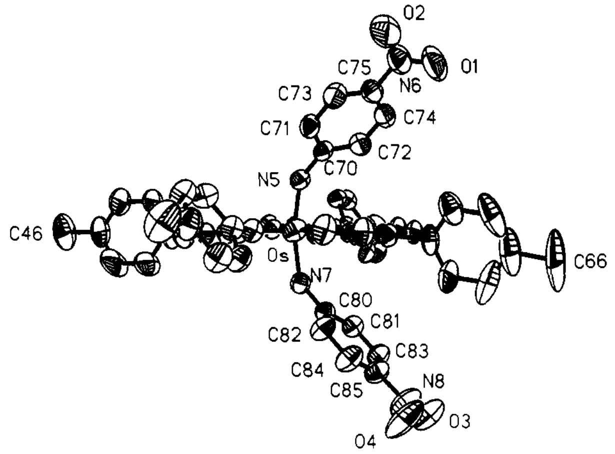

Figure 3. ORTEP drawing of the whole Os(TTP)(p-NC$_6$H$_4$NO$_2$)$_2$ molecule showing the atom-numbering scheme and the tilt of the organoimido ligands.

The organoimido ligands in the new porphyrin complex, Os(TTP)(p-NC$_6$H$_4$NO$_2$)$_2$, are strongly bent with Os–N5–C70 = 144.8(3)° and Os–N7–C80 = 142.0(4)°. Most metal–organoimido bond angles range from 153 to 180°.[24] Linear bonds imply sp hybridization and a M–N triple bond. The smaller bond angles are observed in octahedral compounds that possess multiple π-bonding ligands that must share the three metal π-symmetry orbitals which decreases the M–N bond order. The long bonds and small bond angles in Os(TTP)(p-NC$_6$H$_4$NO$_2$)$_2$ may indicate metal–organoimido bonds that have a significant amount of double-bond character. Studies are in progress to examine the reactivity of these unique osmium–organoimido bonds.

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Supplementary Material Available: Tables giving final values of all refined atomic coordinates, calculated atomic coordinates, anisotropic thermal parameters, and bond lengths and angles (15 pages). Ordering information is given on any current masthead page.

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