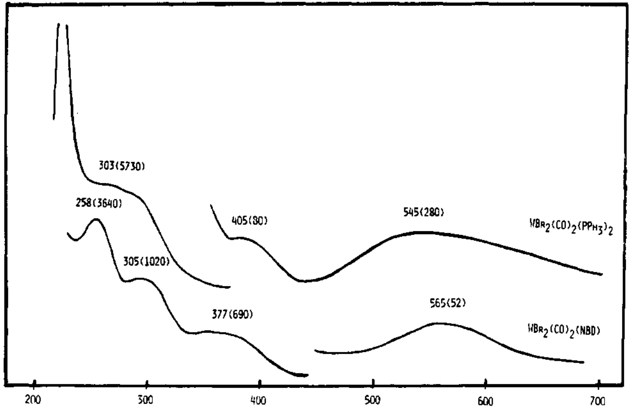

Figure 3. Visible absorption spectra of compounds 1 (lower) and 2 (upper). The wavelength scale is in nanometers, and all absorption maxima are marked with their exact wavelengths and, in parentheses, their molar extinction coefficients.

qualitative discussion, we have carried out a Fenske–Hall calculation using $MoBr_2(CO)_2(H_2C{=}CH_2)_2$ as a model compound. The model was designed to have perfect C_{2v} symmetry with the interatomic distances and angles set equal to the mean values of those found in $WBr_2(CO)_2(C_7H_8)$, except that the angle subtended at the metal atom by the midpoints of the C=C bonds was set at exactly 90°. The planar $H_2C{=}CH_2$ molecules were set precisely perpendicular to the lines from the Mo atom to the midpoints of the C=C bonds. The coordinate axes were chosen with the z axis corresponding to the C_2 axis of symmetry (i.e., bisecting the Br–Mo–Br angle) and the x axis coinciding with a strictly linear OC–Mo–CO chain of atoms.

The results of the FH calculation are summarized in Table VII. A figure showing more of the results, including those for various fragments, is available as supplementary material. These results fully confirm the qualitative analysis. The metal $d\pi$ type orbitals are grouped into a pair of virtually the same energy, $1b_1$ (xz) and $1a_2$ (xy), which are filled, and some 3.3 eV higher in energy, the empty $1a_1$ (z^2) orbital.

Electronic Absorption Spectra. The electronic absorption spectra of both compounds are shown in Figure 3. In each case there is a broad absorption band in the 500–600-nm region. We believe that these bands can be attributed to the transitions from the two highest filled $d\pi$ type orbitals to the lowest unfilled orbital, which is also of $d\pi$ character. The calculations in both cases predict the relevant orbital energy differences to be a little over 3 eV whereas the absorption bands are at about 2 eV. Since FH calculations are known to place virtual orbitals at energies that are too high, the predicted and observed energies are in fair agreement. The transitions involved, two of very similar energy in each case, are all dipole allowed in C_{2v} symmetry. However, to the extent that they retain essentially d → d character, they have a parity-forbidden character. This would explain why their intensities are relatively low.

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Registry No. 1, 93473-77-9; 2, 93601-02-6; $WBr_2(CO)_2(PMe_2Ph)_3$, 47735-34-2; $WBr_2(CO)_2(NBD)(PMe_2Ph)$, 93473-78-0; $MoBr_2(CO)_2(PH_3)_2$, 93473-79-1; $MoBr_2(CO)_2(C_2H_4)_2$, 93473-80-4; $WBr_2(CO)(PMe_2Ph)(NBD)$, 93601-03-7; $WBr_2(CO)_4$, 22172-31-2; NBD, 121-46-0; $WBr_2(CO)_3(PPh_3)_2$, 18130-07-9.

Supplementary Material Available: Lists of structure factors, tables of anisotropic thermal parameters, complete tables of bond lengths and angles, and graphical results of the FH calculations (12 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

Synthesis and Characterization of an Unusual Asymmetric Diosmium Complex, $Os_2Cl_3(PhNpy)_3$

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The title compound was obtained by reaction of $Os_2(O_2CCH_3)_4Cl_2$ with the ligand 2-anilinopyridine in a toluene solution containing trimethylsilyl chloride. The dark blue crystals formed on addition of hexane and subsequent cooling belong to the triclinic system, space group $P\bar{1}$, with unit cell dimensions of a = 9.269 (3) Å, b = 12.023 (2) Å, c = 16.191 (4) Å, α = 90.84 (2)°, β = 100.73 (2)°, γ = 97.01 (2)°, and V = 1758 (1) Å^3 with Z = 2. The structure was refined to R = 0.035 (R_w = 0.047). The complex is unusual in that each osmium atom is in a different environment. The Os–Os distance, 2.392 (1) Å, is the longest yet recorded for a diosmium complex nominally containing a triple bond. The complex is paramagnetic exhibiting a moment of 1.46 μ_B/Os at 308 K. A dichloromethane solution of the complex displays two distinct absorption bands at 868 (ϵ = 1880) and 615 nm (4920) in its electronic spectrum and exhibits both oxidative (+0.75 V) and reductive (−0.23, −0.37, −1.25, −1.47 V) waves when examined by cyclic voltammetry.

Introduction

Although the field of multiply bonded diosmium complexes is a rapidly expanding one, our knowledge of these systems is still very limited.[1] Several complexes of general formula $Os_2(XYZ)_4Cl_2$, where XYZ is a three-atom bridging ligand, have been reported, but the chemistry of these has not as yet been developed in any systematic manner. Complexes are known with the donor sets O,O;[2-5] O,N;[6,7] and P,C.[8] We now report for the first time a triply bonded diosmium complex

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containing a N,N donor set. Recently in this laboratory the 2-anilinopyridinato (PhNPy) ligand has been successfully utilized as a bridging ligand in the quadruply bonded complexes $M_2(PhNPy)_4$ (M = Mo, W),[9] and hence its use with the diosmium unit seemed natural. The molybdenum and tungsten complexes were formed by reactions with the lithium salt of the anion, $PhNpy^-$, formed by deprotonation of PhNHpy. However, from previous experience with diosmium complexes it appeared that a successful synthesis was more likely to result from using a milder reagent to remove the acetato ligands from $Os_2(O_2CCH_3)_4Cl_2$. The method of choice was to remove the acetate anions by reaction with trimethylsilyl chloride in the presence of the potential ligand. However, the product isolated was not of the expected type, namely $Os_2(PhNPy)_4Cl_2$; instead, we obtained a rather more interesting asymmetric complex, $Os_2Cl_3(PhNPy)_3{\cdot}0.25C_7H_8$. In this compound the two osmium ions are inequivalent, one of them being coordinatively unsaturated, and the metal–metal bond is bridged by only three ligands. The complex has been characterized by a number of techniques and the structure of the complex in the solid state determined unequivocally by X-ray crystallography. The complex shows a number of bands in its electronic absorption spectrum in the range 400–900 nm and exhibits a rich electrochemical behavior.

Experimental Section

$Os_2(O_2CCH_3)_4Cl_2$ was prepared by a literature method.[4] All other reagents were purchased from normal commercial suppliers. Solvents used were of analytical grade and were distilled under nitrogen prior to use. All manipulations were carried out under a dinitrogen atmosphere.

Preparation of $Os_2Cl_3(PhNPy)_3{\cdot}0.25C_7H_8$. A 0.10-g quantity of $Os_2(O_2CCH_3)_4Cl_2$ was suspended in 15 mL of toluene. The ligand 2-anilinopyridine, 0.10 g, was added together with 0.15 mL of chlorotrimethylsilane. This mixture was heated to reflux for 4 h after which time a dark blue solution had formed. This solution was cooled and then filtered through Celite. The filtrate was carefully layered with an equal volume of hexane and stored at 0 °C for 48 h. During this time a homogeneous mass of dark crystalline material was deposited. This was isolated by filtration and washed with methanol. The crystalline material is indefinitely stable in air. Yield: 20 mg (13%). Infrared spectrum (Nujol mull, CsI plates): 1599, 1582, 1413, 1341, 1284, 1258, 1202, 1155, 1012, 920, 865, 800, 756, 722, 696, 514, 450, 387, 324, 300, 265, 228 cm^{-1}. Electronic spectrum (900–400 nm, CH_2Cl_2 solvent): λ_{max} 868 nm (ϵ = 1880 M^{-1} cm^{-1}), 615 (4920) 527 (sh). Magnetic moment (CH_2Cl_2): μ_{eff} = 1.46 μ_B/Os (308 K).

Measurements. Infrared spectra were recorded on a Perkin-Elmer 785 spectrometer. Electronic spectra were obtained on a Cary 17D spectrophotometer. Electrochemical measurements were made with a Bioanalytical System, Inc., Model BAS100 electrochemical analyzer instrument in connection with a Bausch & Lomb, Houston Instruments Model DMP 40 digital plotter. Measurements were made in methylene chloride solution containing 0.1 M $(NBu_4)BF_4$ as supporting electrolyte. A three-electrode cell configuration was employed with a platinum disk, Model BAS MF 2032, and platinum wire as working and auxiliary electrodes, respectively, and a BAS MF 2020 Ag–AgCl cell as a reference electrode (against which ferrocene is oxidized at $E_{1/2}$ = +0.52 V). All potentials were referenced to the Ag–AgCl electrode at 22 ± 2 °C with full positive-feedback resistance compensation. Magnetic measurements were made in solution by the Evans method on a Varian EM 390 spectrometer.

X-ray Crystallographic Procedures. Microscopic examination of the crystalline product showed that it was extremely homogeneous, consisting entirely of dark blue crystals that were very uniform in size and general appearance. A typical one was selected, and the structure of the complex was determined by applying the general procedures described elsewhere.[10,11] A detailed description is available as supplementary material. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I.

Table I. Crystallographic Parameters

formula	$Os_2Cl_3N_6C_{34.75}H_{29}$
fw	1016.99
space group	$P\bar{1}$
syst abs	none
a, Å	9.269 (3)
b, Å	12.023 (2)
c, Å	16.191 (4)
α, deg	90.84 (2)
β, deg	100.73 (2)
γ, deg	97.01 (2)
V, Å^3	1758 (1)
Z	2
d_{calcd}, g/cm^3	1.92
cryst size, mm	0.1 × 0.1 × 0.15
μ(Mo Kα), cm^{-1}	74.2
data colln instrum	Syntex P$\bar{1}$
radiation (monochromated in incident beam)	Mo
orientation reflcns: no.; range (2θ), deg	15; $25.2 < 2\theta < 33.8$
temp, °C	5
scan method	ω–2θ
data colln range (2θ), deg	$5 < 2\theta < 50$
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	2761, 2693
no. of parameters refined	397
transmissn factors: max, min	99.93%, 73.55%
R^a	0.035
$R_w{}^b$	0.047
quality-of-fit indicator^c	1.022
largest shift/esd, final cycle	0.03
largest peak, e/Å^3	0.98

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma(|F_o|^2)$. ^{c} Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

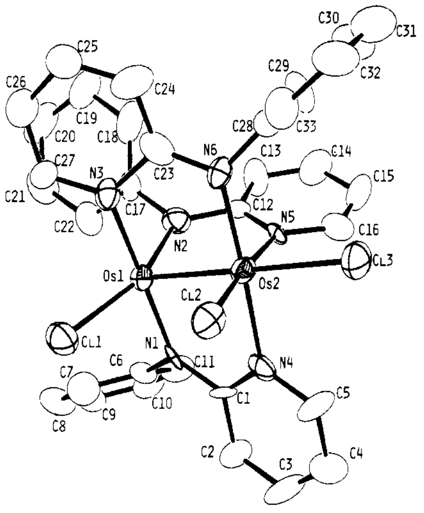

Figure 1. ORTEP drawing of the entire molecule, $Os_2Cl_3(PhNPy)_3$. Atoms are represented by thermal vibration ellipsoids at the 50% level, and the atomic labeling scheme is defined.

The compound crystallizes in the triclinic space group $P\bar{1}$, with the entire molecule as the asymmetric unit. The positions of the metal atoms were derived from a three-dimensional Patterson map, and the remainder of the structure was obtained by using least-squares re-

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Table II. Positional Parameters and Their Estimated Standard Deviations for $Os_2Cl_3(PhNpy)_3\cdot 0.25C_7H_8$

atom	x	y	z	B,[a] Å^2	atom	x	y	z	B,[a] Å^2
Os(1)	0.10248 (7)	0.26405 (5)	0.19260 (4)	2.24 (1)	C(15)	0.645 (2)	0.375 (2)	0.386 (1)	5.3 (5)
Os(2)	0.19260 (7)	0.42538 (5)	0.28428 (4)	2.42 (1)	C(16)	0.500 (2)	0.403 (2)	0.377 (1)	4.4 (5)
Cl(1)	−0.1520 (5)	0.2490 (4)	0.1444 (3)	3.7 (1)	C(17)	0.329 (2)	0.178 (1)	0.124 (1)	2.9 (4)
Cl(2)	−0.0304 (5)	0.5053 (3)	0.2623 (3)	3.5 (1)	C(18)	0.422 (2)	0.229 (2)	0.073 (1)	4.5 (5)
Cl(3)	0.2930 (6)	0.5881 (4)	0.3793 (3)	4.2 (1)	C(19)	0.431 (2)	0.182 (2)	−0.003 (1)	5.4 (5)
N(1)	0.078 (1)	0.1738 (9)	0.2932 (8)	2.0 (3)	C(20)	0.354 (2)	0.073 (2)	−0.026 (1)	5.3 (5)
N(2)	0.310 (1)	0.235 (1)	0.1982 (8)	2.8 (3)	C(21)	0.264 (2)	0.022 (2)	0.026 (1)	5.4 (5)
N(3)	0.124 (1)	0.362 (1)	0.0912 (8)	2.7 (3)	C(22)	0.255 (2)	0.072 (1)	0.104 (1)	3.9 (4)
N(4)	0.116 (1)	0.335 (1)	0.3809 (9)	2.8 (3)	C(23)	0.218 (2)	0.466 (1)	0.105 (1)	2.6 (3)
N(5)	0.393 (1)	0.358 (1)	0.3126 (8)	2.4 (3)	C(24)	0.250 (2)	0.522 (1)	0.033 (1)	4.8 (5)
N(6)	0.263 (1)	0.503 (1)	0.1852 (8)	2.7 (3)	C(25)	0.193 (2)	0.478 (2)	−0.049 (1)	4.6 (5)
C(1)	0.075 (2)	0.222 (1)	0.3696 (9)	2.4 (3)	C(26)	0.105 (2)	0.377 (1)	−0.058 (1)	4.0 (4)
C(2)	0.024 (2)	0.158 (1)	0.435 (1)	3.4 (4)	C(27)	0.069 (2)	0.318 (2)	0.010 (1)	3.4 (4)
C(3)	0.013 (2)	0.214 (2)	0.507 (1)	5.2 (5)	C(28)	0.371 (2)	0.601 (1)	0.197 (1)	3.1 (4)
C(4)	0.054 (2)	0.331 (1)	0.520 (1)	3.9 (4)	C(29)	0.518 (2)	0.584 (2)	0.217 (1)	4.4 (5)
C(5)	0.108 (2)	0.387 (2)	0.457 (1)	3.8 (4)	C(30)	0.629 (2)	0.681 (2)	0.234 (1)	5.9 (6)
C(6)	0.067 (1)	0.055 (1)	0.283 (1)	2.1 (3)	C(31)	0.580 (2)	0.789 (2)	0.229 (1)	5.8 (6)
C(7)	−0.047 (2)	−0.005 (1)	0.227 (1)	4.1 (4)	C(32)	0.428 (2)	0.799 (1)	0.208 (1)	4.7 (5)
C(8)	−0.055 (2)	−0.122 (1)	0.217 (1)	4.3 (5)	C(33)	0.322 (2)	0.704 (1)	0.192 (1)	4.2 (5)
C(9)	0.055 (2)	−0.179 (1)	0.265 (1)	3.9 (4)	C(100)	0.422 (4)	0.944 (3)	0.534 (2)	3.6 (7)*
C(10)	0.171 (2)	−0.118 (1)	0.322 (1)	3.5 (4)	C(102)	0.530 (7)	0.946 (5)	0.482 (4)	3 (1)*
C(11)	0.181 (2)	0.000 (1)	0.331 (1)	3.6 (4)	C(103)	0.519 (7)	1.119 (5)	0.491 (4)	2 (1)*
C(12)	0.426 (1)	0.282 (1)	0.2584 (9)	2.2 (3)	C(104)	0.423 (5)	1.132 (3)	0.544 (3)	5 (1)*
C(13)	0.568 (2)	0.247 (2)	0.265 (1)	4.1 (5)	C(105)	0.349 (8)	1.022 (6)	0.562 (5)	2 (2)*
C(14)	0.681 (2)	0.298 (2)	0.328 (1)	5.0 (5)					

[a] Starred parameters were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table III. Selected Bond Distances (Å) in $Os_2Cl_3(PhNpy)_3\cdot 0.25C_7H_8$

Os(1)-Os(2)	2.392 (1)	N(1)-C(1)	1.36 (2)
Os(1)-Cl(1)	2.326 (5)	-C(6)	1.43 (2)
-N(1)	2.003 (13)	N(2)-C(12)	1.37 (2)
-N(2)	1.986 (14)	-C(17)	1.43 (2)
-N(3)	2.058 (14)	N(3)-C(23)	1.43 (2)
Os(2)-Cl(2)	2.354 (5)	N(4)-C(1)	1.36 (2)
-Cl(3)	2.449 (5)	N(5)-C(12)	1.36 (2)
-N(4)	2.099 (14)	N(6)-C(23)	1.33 (2)
-N(5)	2.093 (13)	-C(28)	1.43 (2)
-N(6)	2.041 (14)		

Table IV. Selected Bond Angles (deg) in $Os_2Cl_3(PhNpy)_3\cdot 0.25C_7H_8$

Os(2)-Os(1)-Cl(1)	112.2 (1)	N(1)-Os(1)-N(2)	93.5 (6)
-N(1)	89.1 (4)	-N(3)	177.7 (5)
-N(2)	88.7 (4)	N(2)-Os(1)-N(3)	88.1 (6)
-N(3)	89.3 (4)	Cl(2)-Os(2)-Cl(3)	85.7 (2)
Os(1)-Os(2)-Cl(2)	96.3 (1)	-N(4)	87.8 (4)
-Cl(3)	178.1 (2)	-N(5)	176.0 (4)
-N(4)	88.0 (4)	-N(6)	93.2 (4)
-N(5)	86.8 (4)	Cl(3)-Os(2)-N(4)	92.0 (4)
-N(6)	88.0 (4)	-N(5)	91.2 (4)
Cl(1)-Os(1)-N(1)	92.2 (4)	-N(6)	92.0 (4)
-N(2)	158.4 (4)	N(4)-Os(2)-N(5)	89.8 (5)
-N(3)	86.9 (4)	-N(6)	175.9 (5)
		N(5)-Os(2)-N(6)	89.4 (5)

finement and difference Fourier maps. In the last few cycles of refinement the presence of a solvent molecule in the unit cell was observed. This was successfully refined as a molecule of toluene disordered over two sites with an occupancy of 0.25 at each.

Table II lists the atomic coordinates and isotropic equivalent thermal parameters, while Tables III and IV contain the important bond distances and angles for the molecule. Complete tables of bond distances and angles as well as anisotropic thermal parameters and structure factors are available as supplementary material.

Figure 1 shows the complete molecule, while Figure 2 shows a view down the Os–Os axis in which only the atoms in the immediate coordination sphere are included.

Results and Discussion

Several years ago the first compound containing a triple bond between osmium ions was discovered in this laboratory.[1,6] Since that time the chemistry of diosmium compounds containing metal–metal triple bonds has undergone considerable development. In addition to the hydroxypyridinate[1,6] and several tetracarboxylates,[2-5] the orthometalated diosmium species, $Os_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2$, has recently been reported.[8] Most recently we have synthesized and characterized, principally by X-ray crystallography, the benzamidato-bridged complexes $Os_2(PhCONH)_4X_2$ (X = Cl, Br).[7] In an effort to extend the range of compounds available, we sought to prepare a complex in which the Os≡Os bond would be bridged by four ligands with N,N donor sets. In view of recent success in preparing the quadruply bonded complexes $M_2(PhNpy)_4$ (M = Mo, W)[9] the ligand of choice was again the anion of 2-anilinopyridine.

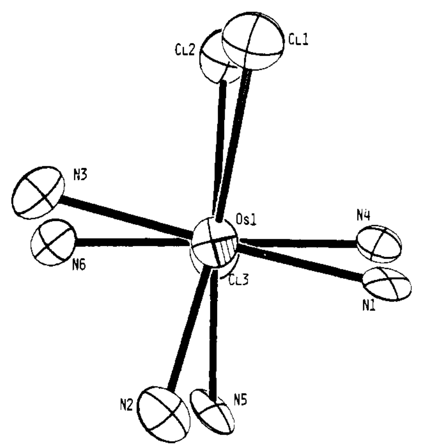

Figure 2. View down the Os≡Os bond showing the immediate coordination sphere. Os(2) lies directly behind Os(1).

The interaction of $Os_2(O_2CCH_3)_4Cl_2$ with this ligand in refluxing toluene containing an excess of trimethylsilyl chloride (to remove acetate groups) rapidly gave rise to an intensely dark blue solution. Filtration, followed by addition of *n*-hexane and cooling, gave a very homogeneous crop of small equidimensional crystals in low yield. These crystals appear to be indefinitely stable in air, and they are soluble in methylene chloride. The intended synthetic target in this preparation was the $Os_2(PhNpy)_4Cl_2$ molecule, but instead the rather more interesting molecule $Os_2Cl_3(PhNpy)_3$ was the isolated product.

The infrared spectrum of the crystalline material contained no bands at 1450 and 1380 cm^{-1} (the asymmetric and symmetric $\nu(CO_2)$ stretches of the acetate precursor) but did exhibit strong bands in the regions 680–770 and 1570–1610 cm^{-1}, which we know to be typical of the 2-anilinopyridinato ligand. The band at 3200 cm^{-1} in PhNHpy itself, due to the ν(N–H) stretch, was also absent in the complex. The acetate complex exhibits only a single ν(Os–Cl) stretch in the region 250–350 cm^{-1}, at 345 cm^{-1} in be precise, whereas the product of this reaction exhibits at least three bands in this region, at 324, 300, and 265 cm^{-1}, indicative of the lower symmetry in this complex. Attempts to observe proton NMR signals from a solution of the complex in CD_2Cl_2 were unsuccessful, presumably because of the paramagnetic nature of the product, discussed below.

Unequivocal determination of the structure was provided by an X-ray crystallographic analysis that showed the complex to be an asymmetric molecule, $Os_2Cl_3(PhNpy)_3$, in which the metal–metal bond is spanned by three bridging ligands. The synthesis of such a species is not unprecedented, the quadruply bonded rhenium complex $Re_2Cl_3[O_2CC(CH_3)_3]_3$, for example, having been reported several years ago.[12] However, that complex was polymeric in the solid state, whereas each $Os_2Cl_3(PhNpy)_3$ molecule is discrete.

The unsymmetrical arrangement of ligands of course makes the two metal atoms nonequivalent, but in a formal sense their oxidation states may be the same. If we assume that the −1 valence of the $PhNpy^-$ ligand is centered on the anilino nitrogen atom, we then see that Os(1) is bonded to one Cl^- and two N^- ligand atoms while Os(2) is bonded to one N^- and two Cl^- ligand atoms.

The structure consists of a dinuclear osmium core bridged by three 2-anilinopyridinato ligands, with the fourth equatorial position on each metal occupied by a chloride ion. One osmium atom has in addition an axial chloride ligand. The osmium–osmium distance, 2.392 (1) Å, is the longest one so far observed for this class of diosmium complexes, which may, perhaps, be attributed to the repulsive interactions between the chloride ligands, Cl(1) and Cl(2). The axial Os(2)–Cl(3) bond has a length of 2.449 (5) Å while the axial position on the other metal is vacant and somewhat encumbered by the phenyl rings of two of the bridging 2-anilinopyridinato ligands. The equatorial chloride ions have bond distances, Os(1)–Cl(1) = 2.326 (5) and Os(2)–Cl(2) = 2.354 (5) Å, that are significantly shorter than the bond distance to the axial chloride, as might have been expected. The coordination about the metal ions is approximately octahedral with the exception that angles to Cl(1) and Cl(2) are significantly greater than 90°, viz., Os(2)–Os(1)–Cl(1) = 112.2 (1) and Os(1)–Os(2)–Cl(2) = 96.3 (1)°. The Os(1)–Os(2) and Os(2)–Cl(3) bonds are almost collinear, Os(1)–Os(2)–Cl(3) = 178.1 (2)°. The separation between Cl(1) and Cl(2) is 3.55 Å. The bonds to the nitrogen atoms fall in the range 1.98–2.10 Å with no statistically significant difference in the mean Os–N(amine), 2.043 (14) Å, and Os–N(pyridine), 2.083 (14) Å, distances. There are significant torsion angles about the metal–metal bond, as can be seen Figure 2. These torsion angles are as follows: Cl(1)–Os(1)–Os(2)–Cl(2), 8.1°; N(1)–Os(1)–Os(2)–N(4), 12.5°; N(2)–Os(1)–Os(2)–N(5), 16.1°; N(3)–Os(1)–Os(2)–N(6), 14.7°. In view of the low symmetry of the molecule, the complexity of the infrared spectrum in the region 250–350 cm^{-1} is not surprising.

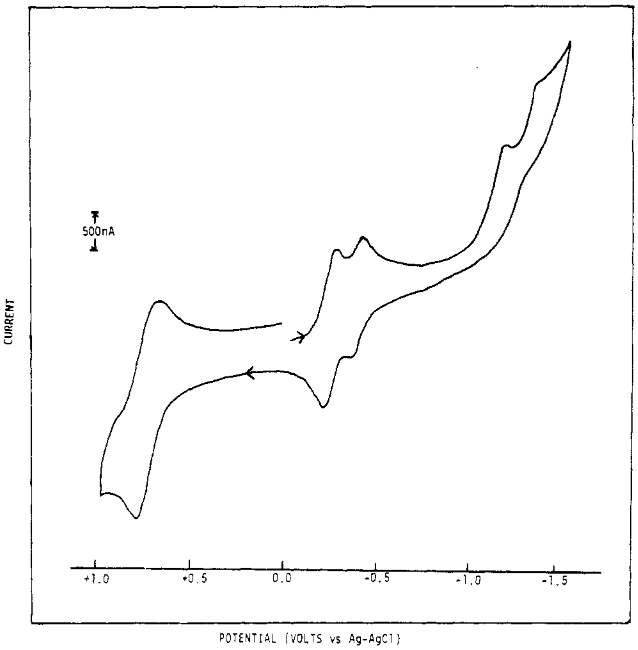

Figure 3. Cyclic voltammogram for $Os_2Cl_3(PhNpy)_3$ in CH_2Cl_2 (0.1 M tetrabutylammonium tetrafluoroborate), potential sweep rate 100 mV s^{-1}.

Since paramagnetism is exhibited by the vast majority of triply bonded diosmium complexes, it was not surprising that magnetic measurements made at 308 K on dichloromethane solutions of the complex (by Evans' method[13]) show that this species is also paramagnetic. The magnitude of μ_{eff}, 2.07 μ_B (1.46 μ_B/Os), is consistent with the previously reported values for the carboxylates and $Os_2(hp)_4Cl_2$.[4] Hence, it seems likely that in this complex also there is an appreciable population of a spin triplet state (perhaps corresponding to the electronic configuration $\sigma^2\pi^4\delta^2\pi^{*2}$ or $\sigma^2\pi^4\delta^2\delta^*\pi^*$) at ambient temperature, with the singlet ground state (arising from the $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration) becoming increasing favored at lower temperatures.

Although the carboxylates are paramagnetic, the complex $Os_2(O_2CC_3H_7)_4Cl_2$ showed sharp, contact-shifted signals in both carbon-13 and hydrogen-1 NMR spectra.[4] The explanation for our inability to observe ^1H NMR signals in this complex may be that the π bonding in both the pyridine and aniline rings results in significantly greater delocalization of the unpaired electron density and hence very broad NMR lines.

The electronic spectrum (900–400 nm) of a dichloromethane solution of the complex shows two distinct bands, at 868 nm (1880) and 615 nm (4920). In addition, a broad shoulder is apparent at 527 nm, while a third weak peak, which can only just be distinguished from the background, is observed at ca. 455 nm. In view of the paucity of data and the probable equilibrium between singlet and triplet states, we feel it would be premature to attempt an assignment of the electronic spectrum at this stage. Clearly, both single-crystal spectroscopic studies and semiempirical calculations will be necessary before we can begin to gain an insight into the behavior of this complex system.

In view of the rich electrochemical behavior of both $Os_2(O_2CR)_4Cl_2$ (R = C_2H_5, C_3H_7)[14] and $Os_2(hp)_4Cl_2$,[15] it was decided to investigate the redox behavior of this asymmetric complex. Investigations were made in dichloromethane so-

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[14] R = C_2H_5: reversible reduction, +0.57 V; irreversible reduction, −1.32 V; irreversible oxidation, +1.89 V. R = C_3H_7: reversible reduction, +0.53 V; irreversible reduction, −1.00 V; irreversible oxidation, +1.84 V.

[15] Quasi-reversible reduction, +0.26 V; quasi-irreversible oxidation, +1.36 V.

lution using 0.1 M $(Bu_4N)BF_4$ as the supporting electrolyte and an Ag–AgCl reference electrode by both the cyclic voltametric and differential-pulse techniques.

The complex exhibits a number of waves on the cyclic voltametric time scale as shown in Figure 3. A quasi-reversible oxidation wave is evident at +0.75 V (peak to peak separation, $\Delta E_p = 70$ mV) with a current ratio i_c/i_a of ca. 1. When the scan rate is increased to 2000 mV s^{-1}, the i_c/i_a ratio decreases with a concomitant increase in ΔE_p. In addition, at fast scan rates the development of a further reduction wave is observed at $E_{p,c}$ ca. +0.60 V. These observations are consistent with an equilibrium between the oxidized product and a second redox-active species that is reduced independently. A number of reduction processes are evident. There are two quasi-reversible reduction waves, at −0.23 and −0.37 V, with $\Delta E_p \approx 60$ mV for both, but with an i_a/i_c ratio $\ll 1$. Upon further increase of the scan rate, the i_a/i_c ratio approaches unity for the more facile reduction, with no apparent change in the ratio for the second reduction. This effect was also observed upon recording the voltammagram in increasingly dilute solution. The interpretation of these observations is not at this stage apparent. However, a possible explanation for the two waves is that we are observing a sequential reduction of the two ends of the asymmetric molecule. In addition to these quasi-reversible processes, two further multielectron reduction processes are observed at potentials of −1.25 and −1.47 V.

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Registry No. $Os_2Cl_3(PhNpy)_3 \cdot 0.25C_7H_8$, 93606-10-1; $Os_2(O_2CCH_3)_4Cl_2$, 81519-41-7; Os, 7440-04-2.

Supplementary Material Available: Details of the crystal structure determination and listings of bond angles, anisotropic thermal parameters, bond distances, and observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
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An Ortho-Metalation Reaction of $Os_2(O_2CCH_3)_4Cl_2$: Syntheses and Crystal Structure Characterizations of $Os_2(O_2CR)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2$ (R = CH_3 (1), C_2H_5 (2))

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The compounds $Os_2(O_2CR)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2$ (R = CH_3 (**1**), C_2H_5 (**2**)) have been prepared by the interaction of $Os_2(O_2CCH_3)_4Cl_2$ with triphenylphosphine in the appropriate carboxylic acid. Each molecule consists of a diosmium unit bridged by two cisoid carboxylato ligands and by triphenylphosphine ligands in which ortho metalation has occurred at one of the phenyl rings on each phosphine. The black crystals of the acetate, **1**, belong to the monoclinic system, space group *C*2/*c*, with unit cell dimensions $a = 16.315$ (6) Å, $b = 14.210$ (4) Å, $c = 19.271$ (9) Å, $\beta = 109.34$ (3)°, and $V = 4211$ (2) Å^3 with $Z = 4$. The propionate, **2**, crystallized in the orthorhombic space group *Pbcn* with unit cell dimensions $a = 11.901$ (2) Å, $b = 18.473$ (5) Å, $c = 17.578$ (6) Å, and $V = 3864$ (2) Å^3 with $Z = 4$. The structure of **1** was refined to $R = 0.030$ ($R_w = 0.040$) while **2** gave $R = 0.027$ ($R_w = 0.039$). The Os≡Os distances 2.271 (1) and 2.272 (1) Å, for **1** and **2**, respectively, are the shortest yet recorded for a diosmium complex containing a triple bond. In each case the molecule has crystallographic C_2 symmetry; the inner group of atoms, i.e., the two Os atoms and the $P_2C_2O_4Cl_2$ group bonded to them, show no higher symmetry since there is a significant twist about the Os–Os axis away from an eclipsed geometry and the Cl–Os–Os–Cl chains are far from linear, with Cl–Os–Os angles of 161.08 (5)° in **1** and 162.51 (5)° in **2**. In contrast to their $Os_2(O_2CR)_4Cl_2$ precursors, these complexes are essentially diamagnetic.

Introduction

In the developing chemistry of compounds containing multiple bonds between atoms of the transition metals,[1] two important goals have always been (1) the enlargement of the number of compounds with metals other than Mo and Re, which were first extensively exploited, and (2) the discovery of new classes of bridging ligands. For a number of years, specific objectives, both of this group and elsewhere, have been the discovery of new diosmium compounds and the preparation of complexes containing a metal–metal bond that is bridged by an ortho-metalated ligand. Since ortho-metalation reactions are by no means uncommon at single metal centers it is perhaps surprising that M_2 complexes containing bridging ortho-metalated ligands have been so elusive. The first[2] report of a complex of this type, $Re_2Cl_3(Ph_2Ppy)_2[(C_6H_5)(C_6H_4)Ppy]$,[2,3] appeared only in 1983. The ortho-metalated ligand, 2-(diphenylphosphino)pyridine, in this complex exhibited an unusual tridentate mode of coordination and therefore could not be regarded as a typical or prototypal ortho-metalated bridging ligand. In the course of our investigations into the reactivity of the recently reported osmium carboxylates,[4–7] we were able to prepare the complex $Os_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2Cl_2$.[8] We have now found that, in contrast to the synthesis of the rhenium complex, the synthetic method by which this diosmium compound was obtained can be readily generalized to include other carboxylic acids and transition-metal ions, and a number of ortho-metalated dirhodium complexes, $Rh_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2 \cdot 2L$,[8,9] have been prepared.

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