1334 *Inorg. Chem.* **1985**, *24*, 1334-1338

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Syntheses and Molecular Structures of $Os_2X_2(PhCONH)_4$ (X = Cl, Br) Compounds

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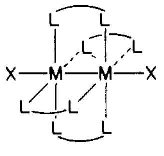
Received June 28, 1984

The compound $Os_2Cl_2(PhCONH)_4$ (**1**) was prepared by reacting $Os_2Cl_2(O_2CCH_3)_4$ with benzamide at 140 °C. The dibromo analogue (**2**) was obtained by adding a tetraalkyl bromide salt to a solution of **1** in Me_2SO. Both compounds are dark green in color, soluble in Me_2SO, but only sparingly soluble or insoluble in other common organic solvents. Both compounds are indefinitely stable in air. The molecular structures of both the compounds, which are isomorphous, were obtained by X-ray crystallography. They crystallize in the triclinic space group $P\bar{1}$ with 2 molecules per unit cell. The molecules have a center of inversion, and thus the asymmetric unit consists of half of each of two dinulcear molecules at 0, 0, 0 and $^1/_2$, $^1/_2$, $^1/_2$. The unit cell dimensions are as follows: $Os_2Cl_2(PhCONH)_4$, $a = 10.840$ (6) Å, $b = 14.381$ (7) Å, $c = 10.682$ (7) Å, $\alpha = 110.91$ (4)°, $\beta = 105.80$ (6)°, $\gamma = 68.10$ (6)°, $V = 1424$ (1) Å^3; $Os_2Br_2(PhCONH)_4$, $a = 10.918$ (7) Å, $b = 14.663$ (6) Å, $c = 10.497$ (8) Å, $\alpha = 108.18$ (3)°, $\beta = 106.13$ (7)°, $\gamma = 68.65$ (6)°, $V = 1461$ (1) Å^3. The structures of **1** and **2** were refined to $R = 0.074$ ($R_w = 0.083$) and $R = 0.074$ ($R_w = 0.086$), respectively. The mean $Os\equiv Os$ distances in **1** and **2** are 2.367 [2] and 2.384 [2] Å, respectively. The mean Os–Cl and Os–Br distances are 2.490 [9] and 2.611 [5] Å, respectively. The electronic spectra of these compounds show low-energy bands at 762 and 643 nm in CH_2Cl_2. $Os_2Cl_2(PhCONH)_4$ has a magnetic moment of 1.76 μ_B at 25 °C and undergoes one-electron reduction at −0.07 V vs. SCE in Me_2SO.

Introduction

In the chemistry of transition-metal complexes having metal–metal multiple bonds, one of our prime interests is to investigate the effect of equatorial and axial ligands in species of type I on



I

(i) the electronic structure of the compound and (ii) the metal–metal bond length. Though there has been extensive study of the groups 6 and 7[15] metal triads,[1] the later transition metals were rather neglected for several years. Recently, we have directed our efforts to develop the chemistry of diruthenium and diosmium complexes. From our current studies it is evident that it will be possible to develop an extensive chemistry for diruthenium and diosmium complexes, perhaps, in time, rivaling that known for the elements Cr, Mo, W, Tc, and Re. In this paper we are concerned with a significant extension of the chemistry of diosmium(III).

The first report[2] on a diosmium complex, $Os_2Cl_2(hp)_4$ (Hhp = 2-hydroxypyridine), having an $Os\equiv Os$ bond appeared from this laboratory. A little later, the syntheses, characterizations, and structures of the $Os_2Cl_2(O_2CR)_4$ compounds were reported[3-6] by several groups. Work from this laboratory has shown that the bridging carboxylates can be replaced by other bridging ligands, and we have reported[7,8] the structures of the ortho-metalated species $Os_2Cl_2(O_2CR)_2[Ph_2P(C_6H_4)]_2$[7] and of an unsymmetrical compound $Os_2Cl_3(PhNpy)_3$.[8]

We now report the syntheses, properties, and molecular structures of two diosmium(III) complexes of the benzamidato ligand. Though the reaction between $Os_2Cl_2(O_2C\text{-}n\text{-}Pr)_4$ and 2,2,2-trifluoroacetamide is known[5] to produce an insoluble complex of the type $[Os(ONHCCF_3)_2Cl]_n$, neither the structure nor the physicochemical properties of this complex have been reported. Our work on the present complexes thus provides the first complete characterization of a new class of compound containing amidato bridging ligands, $Os_2X_2(PhCONH)_4$ (X = Cl, Br), by X-ray and other methods. This also gives us an opportunity to study the influence of the bridging ligands on the $Os\equiv Os$ triple bond. It is also noteworthy that the dibromo complex is the first Os_2^{6+} species having axial ligands other than chloride ions. A preliminary report[9] on the X-ray structure of $Os_2Cl_2(PhCONH)_4$ has been made. A correlation between the formal reduction potentials and the $Os\equiv Os$ triple-bond length has also been observed and will be discussed.

Experimental Section

Chemicals. $Os_2Cl_2(O_2CCH_3)_4$ was prepared from OsO_4 (Johnson-Matthey) by a literature method.[5] Benzamide was purchased from Aldrich Chemical Co.

Preparation of $Os_2Cl_2(PhCONH)_4$ (1). A 0.2-g quantity (0.290 mmol) of $Os_2Cl_2(O_2CCH_3)_4$ was mixed with 10 g (82.6 mmol) of benzamide in a sublimer flask. The flask was degassed and subsequently kept under a dinitrogen atmosphere. The flask was then immersed in an oil bath, and the reaction mixture was heated at 140–150 °C. At this temperature the ligand was in the molten state. The heating was continued for 72 h to ensure complete substitution of acetate by the benzamido ligand. During this period the mixture was stirred magnetically. The brown color of the starting material slowly turned to green during the reaction. After 72 h, the excess ligand was removed by sublimation at 140 °C under high vacuum with a dry ice–acetone mixture in the cold finger of the sublimer. The crude product was washed several times with benzene and finally with diethyl ether to remove unreacted ligand. The resulting solid was green in color. The yield was quantitative. The product was recrystallized by slow diffusion of methanol (containing $(C_2H_5)_4NCl$) into a Me_2SO solution of the product. The isolated yield of the crystalline product was 60%.

Anal. Calcd for $Os_2Cl_2O_4N_4C_{28}H_{24}$: C, 36.09; H, 2.58; N, 6.02; Cl, 7.63. Found: C, 36.06; H, 2.57; N, 5.93; Cl, 7.52. The compound is highly soluble in Me_2SO, fairly soluble in CH_3OH, CH_3COCH_3, and CH_2Cl_2, sparingly soluble in diethyl ether and benzene, and insoluble in hexane.

Preparation of $Os_2Br_2(PhCONH)_4$ (2). A 0.04-g quantity of $Os_2Cl_2(PhCONH)_4$ was dissolved in 10 mL of Me_2SO. The solution was filtered (to remove any undissolved compound) into a test tube. A 15-mL solution of CH_3OH containing 0.1 g of tetramethylammonium bromide was slowly added on the top of the Me_2SO solution, maintaining the interface, insofar as possible, undisturbed. Slow diffusion of the solvents led to the formation of a homogeneous crystalline mass in ca. 30% yield. The solubility properties of this compound are about the same as those of **1**.

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0020-1669/85/1324-1334$01.50/0

Table I. Crystallographic Data

compd	$Os_2Cl_2(PhCONH)_4$	$Os_2Br_2(PhCONH)_4$
formula	$Os_2Cl_2O_4N_4C_{28}H_{24}$	$Os_2Br_2O_4N_4C_{28}H_{24}$
fw	931.38	1020.75
space gp	$P\overline{1}$	$P\overline{1}$
syst abs	none	none
a, Å	10.840 (6)	10.918 (7)
b, Å	14.381 (7)	14.663 (6)
c, Å	10.682 (7)	10.497 (8)
α, deg	110.91 (4)	108.18 (3)
β, deg	105.80 (6)	106.13 (7)
γ, deg	68.10 (6)	68.65 (6)
V, Å^3	1424 (1)	1461 (1)
Z	2	2
d_{calcd}, g/cm^3	2.170	2.286
cryst size, mm	0.15 × 0.10 × 0.10	0.20 × 0.15 × 0.10
μ(Mo Kα), cm^{-1}	91.43	112.81
data colln instrum	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.710 73 Å) graphite monochromated	
orientation reflcns; no.; range (2θ), deg	25; 4.5–31.7	25; 6.2–30.3
temp, °C	25	25
scan method	ω–2θ	ω–2θ
data colln range (2θ), deg	5–55	4–50
no. of unique data; total with $F_o^2 > 3\sigma(F_o^2)$	2192; 1601	4924; 2047
no. of parameters refined	256	291
transmissn factors (%): max, min	98.52, 53.17	99.50, 79.69
R^a	0.074	0.074
$R_w{}^b$	0.083	0.086
quality-of-fit indicator^c	1.96	1.81
largest shift/esd, final cycle	0.54	0.06

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

The infrared spectra of the two compounds in KBr phase are essentially identical with only one exception. The band observed at 285 cm^{-1} in **1** is absent in the IR spectrum of **2**. Other bands: 3318 m, 3190 m, 3020 w, 1595 s, 1500 s, 1440 vs, 1235 s, 1185 m, 1155 w, 1112 s, 1025 s, 1000 s, 840 s, 695 vs, 542 s, 470 m, 410 w, 395 w cm^{-1} (vs, very strong; s, strong; m, medium; w, weak).

The electronic spectra of the compounds show bands at 635 nm (ϵ = 1665 M^{-1} cm^{-1}) and 1050 (ϵ = 1050) in Me_2SO. In CH_2Cl_2, $Os_2Cl_2(PhCONH)_4$ exhibits bands at 762 nm (840), 643 (1360), 410 (sh), and 345 (sh) and $Os_2Br_2(PhCONH)_4$ displays bands at 762 nm (850), 643 (1290), 427 (5850), and 350 (7400) (sh = shoulder).

Measurements. The elemental analysis of **1** was obtained from Galbraith Laboratories, Inc. The infrared spectra were recorded with a Perkin-Elmer 785 spectrophotometer. Electronic spectra were obtained by using a Cary 17D spectrophotometer. Electrochemical measurements were carried out with a Beckman Electroscan 30 analytical system. Dimethyl sulfoxide and 0.1 M tetrabutylammonium perchlorate (TBAP) were used as solvent and supporting electrolyte, respectively. The measurements were made under a dinitrogen atmosphere. In the three-electrode system, a planar Beckman Model 39273 platinum-inlay working electrode, platinum-wire auxiliary electrode, and a saturated calomel reference electrode (SCE) were used. Electrochemical measurements were made at 298 K and are uncorrected for junction potentials.

The magnetic susceptibility of **1** was measured by the Faraday method at 25 °C by Dr. Bennett B. Hutchinson of Abiline Christian University. The gram susceptibility was 1.07 × 10^{-6} cgsu from which a corrected molar susceptibility and magnetic moment of 1.30 × 10^{-3} cgsu and 1.76 μ_B were calculated.

X-ray Crystallographic Procedures. The structures of **1** and **2** were obtained by using the same general procedures as described elsewhere.[10,11] A detailed description relevant to these compounds is available as supplementary material. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I. Complete tables of anisotropic thermal parameters and structure factor data are available as supplementary material.

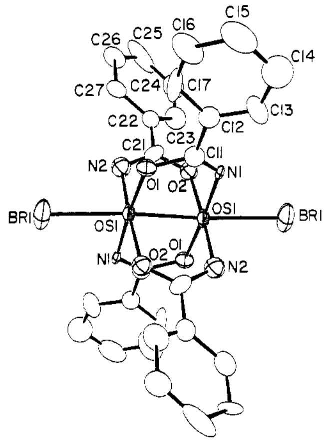

Figure 1. ORTEP drawing at the 50% probability level of one molecule of $Os_2Br_2(PhCONH)_4$ (**2**). The other molecule in the asymmetric unit is essentially identical with this molecule, and the molecules of **1** correspond closely and are numbered analogously.

Compounds **1** and **2** crystallize as dark green crystals in the triclinic system. All diffraction data on both the crystals were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation. Accurate cell dimensions were obtained by indexing 25 reflections from the SEARCH routine. Intensities were measured by the ω–2θ scan technique, and an empirical absorption correction was determined for these crystals by using a ψ scan for each of nine reflections near χ = 90°. The structures were solved first by obtaining the atomic coordinates of the osmium atoms from the Patterson map and then by subsequent use of difference Fourier maps and least-squares refinements. During refinement it was found that the benzamide ligands are slightly disordered. Thermal parameters of some of the atoms were nonpositive definite when refined anisotropically; they were kept isotropic throughout the least-squares refinements. The problem of choosing the N and O atoms of the benzamide ligands were handled by monitoring their isotropic thermal parameters. For example, in the case of $Os_2Br_2(PhCONH)_4$ when the O(1), N(1) positions were interchanged, the thermal parameters after refinement were N(1) = 0.96, O(1) = 3.43. A change in positions of the O(2), N(2) pair gave the B_{iso} values as N(2) = 0.82, O(2) = 5.87. Similarly, exchanges of the O(3), N(3) and O(4), N(4) pairs of atoms resulted in thermal parameters of N(3) = 1.46, O(3) = 4.82 and N(4) = 0.43, O(4) = 4.17. The present arrangement of ligands as shown in Figure 1 gave the best results among all possible combinations. With anisotropic thermal parameters for the Os, Cl, and Br and for some of the N, O, and C atoms, the final refinement converged with R_1 = 0.074 for both complexes with the weighted R factors being 0.083 and 0.086, respectively, for **1** and **2**. The final difference Fourier maps were featureless except for a few peaks around the two metal centers, with Os peak separations being <1.2Å. The highest peak was 2.5 e/Å^3, and it was situated midway between two metal centers. We made no effort to find and to refine any hydrogen atoms because of the presence of intrinsic disorder in these molecules. The presence of some peaks in the final difference Fourier near the metal centers is not unexpected in view of the high values of the linear absorption coefficients (see Table I).

Results and Discussion

Preparation. $Os_2Cl_2(PhCONH)_4$ (**1**) is prepared in quantitative yield by reacting $Os_2Cl_2(O_2CCH_3)_4$ with excess molten benzamide at 140 °C. The excess ligand can easily be removed by sublimation. The dibromo analogue is obtained by adding a methanolic solution of tetramethylammonium bromide to a Me_2SO solution of **1**. The complexes are freely soluble only in Me_2SO and are slightly soluble, or insoluble, in common organic solvents. They are indefinitely stable in air.

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(10) Calculations were done on the VAX-11/780 computer at the Department of Chemistry, Texas A&M University, College Station, TX, with a VAX-SDP software package.

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Table II. Positional Parameters and Their Estimated Standard Deviations for $Os_2Cl_2(PhCONH)_4$ (**1**)

atom	*x*	*y*	*z*	*B*,[a] Å^2
Os(1)	0.0935 (2)	0.0292 (1)	0.0618 (2)	1.99 (4)
Os(2)	1.0364 (2)	0.4500 (1)	0.3939 (2)	3.94 (5)
Cl(2)	0.866 (1)	0.6412 (7)	0.818 (1)	4.3 (3)
Cl(1)	−0.285 (1)	−0.0940 (8)	−0.211 (1)	6.0 (4)
O(1)	−0.191 (2)	0.116 (2)	−0.085 (3)	3.1 (6)*
O(2)	−0.028 (2)	−0.067 (2)	−0.232 (3)	3.6 (6)*
O(3)	1.090 (2)	0.433 (1)	0.685 (2)	3.2 (7)
O(4)	1.110 (2)	0.617 (2)	0.657 (3)	4.0 (6)*
N(1)	0.012 (3)	−0.170 (2)	−0.034 (3)	2.7 (7)*
N(2)	−0.154 (2)	0.010 (2)	0.117 (3)	1.8 (6)*
N(3)	0.848 (3)	0.668 (2)	0.522 (3)	2.2 (8)
N(4)	0.822 (3)	0.477 (2)	0.550 (3)	2.7 (7)*
C(11)	−0.136 (4)	0.187 (3)	−0.036 (4)	4 (1)*
C(12)	−0.214 (4)	0.291 (3)	−0.066 (5)	5 (1)*
C(13)	−0.149 (4)	0.355 (2)	−0.058 (5)	5 (1)
C(14)	0.221 (6)	0.552 (3)	0.088 (6)	8 (2)
C(15)	0.359 (6)	0.528 (3)	0.134 (5)	8 (2)
C(16)	0.421 (6)	0.594 (4)	0.137 (6)	8 (2)*
C(17)	0.357 (5)	0.690 (3)	0.101 (5)	6 (1)*
C(21)	0.085 (3)	−0.050 (2)	−0.227 (4)	2.2 (8)*
C(22)	0.147 (4)	−0.081 (3)	−0.360 (4)	4 (1)
C(23)	0.079 (4)	−0.134 (3)	−0.477 (5)	5 (1)*
C(24)	0.116 (5)	0.840 (4)	0.393 (6)	8 (2)*
C(25)	0.211 (4)	0.881 (3)	0.402 (5)	5 (1)*
C(26)	0.731 (5)	0.058 (4)	0.489 (6)	8 (2)
C(27)	0.757 (4)	0.038 (3)	0.362 (4)	5 (1)
C(31)	0.846 (4)	0.650 (3)	0.393 (4)	4 (1)
C(32)	0.749 (4)	0.726 (3)	0.318 (4)	5 (1)
C(33)	0.629 (5)	0.812 (3)	0.377 (6)	9 (2)
C(34)	0.552 (4)	0.879 (5)	0.298 (5)	8 (2)
C(35)	0.568 (5)	0.870 (4)	0.186 (6)	7 (1)*
C(36)	0.683 (5)	0.788 (4)	0.119 (6)	8 (2)*
C(37)	0.769 (4)	0.720 (4)	0.194 (5)	5 (2)
C(41)	0.806 (4)	0.408 (3)	0.437 (4)	4 (1)*
C(42)	0.697 (3)	0.367 (2)	0.389 (4)	2.8 (8)*
C(43)	0.676 (4)	0.309 (3)	0.248 (5)	4 (1)
C(44)	0.565 (4)	0.261 (3)	0.201 (5)	5 (1)*
C(45)	0.492 (4)	0.269 (3)	0.295 (4)	3.5 (9)*
C(46)	0.517 (5)	0.325 (4)	0.423 (6)	8 (2)
C(47)	0.376 (5)	0.632 (3)	0.533 (5)	6 (1)*

[a] Starred values indicate atoms 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. Positional Parameters and Their Estimated Standard Deviations for $Os_2Br_2(PhCONH)_4$ (**2**)

atom	*x*	*y*	*z*	*B*,[a] Å^2
Os(1)	0.0927 (2)	0.0292 (1)	0.0615 (2)	2.19 (3)
Os(2)	0.9650 (2)	0.5459 (1)	0.6055 (2)	2.44 (4)
Br(1)	0.2868 (4)	0.0985 (3)	0.2188 (5)	4.7 (1)
Br(2)	−0.1298 (5)	−0.3649 (3)	−0.1724 (5)	5.0 (1)
O(1)	−0.165 (2)	0.009 (2)	0.111 (2)	2.9 (7)
O(2)	0.195 (2)	−0.111 (2)	0.084 (2)	2.7 (5)*
O(3)	0.081 (2)	−0.557 (2)	−0.310 (2)	5.1 (7)
O(4)	0.891 (2)	0.390 (2)	0.339 (2)	2.2 (5)*
N(1)	0.018 (2)	0.059 (2)	0.226 (2)	1.5 (7)
N(2)	−0.015 (3)	0.162 (2)	0.033 (3)	3.0 (7)*
N(3)	0.852 (3)	0.652 (2)	0.507 (3)	2.4 (6)*
N(4)	−0.176 (3)	−0.522 (2)	−0.449 (3)	2.1 (6)*
C(11)	−0.087 (3)	0.051 (3)	0.229 (4)	2.9 (8)*
C(12)	0.142 (3)	−0.076 (3)	−0.359 (4)	2.9 (8)*
C(13)	0.086 (4)	−0.131 (3)	−0.469 (4)	5 (1)
C(14)	0.131 (5)	−0.160 (3)	−0.593 (5)	6 (1)*
C(15)	0.231 (5)	−0.115 (3)	−0.592 (5)	6 (2)
C(16)	−0.289 (5)	0.062 (4)	0.477 (4)	8 (2)
C(17)	−0.242 (4)	0.038 (3)	0.368 (4)	7 (1)
C(21)	0.142 (4)	−0.180 (3)	0.040 (4)	4 (1)
C(22)	−0.235 (4)	0.284 (3)	−0.073 (4)	4 (1)
C(23)	0.358 (4)	−0.302 (3)	0.105 (4)	4 (1)
C(24)	0.438 (5)	−0.391 (3)	0.145 (5)	5 (2)
C(25)	0.373 (6)	−0.465 (4)	0.138 (5)	8 (2)
C(26)	0.241 (5)	−0.445 (3)	0.101 (4)	7 (2)
C(27)	0.166 (5)	−0.355 (3)	0.065 (4)	7 (1)
C(31)	0.845 (3)	0.648 (3)	0.388 (3)	3.2 (9)
C(32)	1.250 (3)	0.275 (3)	0.693 (4)	4 (1)
C(33)	1.231 (4)	0.277 (3)	0.818 (4)	4 (1)
C(34)	1.320 (4)	0.206 (4)	0.894 (5)	7 (2)
C(35)	0.577 (4)	0.865 (3)	0.160 (4)	4 (1)
C(36)	1.441 (4)	0.129 (3)	0.712 (5)	5 (1)*
C(37)	1.360 (4)	0.196 (3)	0.634 (4)	3.5 (9)*
C(41)	0.806 (3)	0.419 (2)	0.428 (3)	2.5 (8)*
C(42)	0.693 (4)	0.371 (3)	0.382 (4)	2.9 (8)*
C(43)	0.617 (4)	0.376 (3)	0.468 (4)	4 (1)*
C(44)	0.525 (4)	0.325 (3)	0.435 (5)	7 (1)
C(45)	0.498 (4)	0.272 (3)	0.301 (5)	6 (2)
C(46)	0.571 (4)	0.269 (3)	0.209 (6)	7 (2)
C(47)	0.679 (5)	0.311 (3)	0.253 (5)	5 (1)*

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

Comparison of the IR spectra of **1** and **2** suggests that a band observed in the dichloro species at 285 cm^{-1}, but absent in the dibromo analogue, can probably be assigned to the Os–Cl stretch. The bands at 3318 and 3190 cm^{-1} are possibly due to N–H stretching vibrations. The appearance of two such bands is consistent with the presence of two crystallographically nonequivalent molecules in the unit cell. Significant intramolecular coupling of N–H stretches through the heavy central set of atoms seems unlikely. The bands at 1595 and 1500 cm^{-1} can be tentatively assigned to the antisymmetric and symmetric O–C–N stretches, respectively. In $Os_2(O_2CMe)_4Cl_2$, the bands at 392 and 345 cm^{-1} have been previously assigned[5] to the Os–O and Os–Cl stretches, respectively. The band at 395 cm^{-1} in **1** and **2** could be due to Os–O stretching. The considerable shift of the Os–Cl stretch from 345 to 285 cm^{-1} on going from carboxylato to amidato complexes indicates the weakening of the Os–Cl bond.

Molecular Structures. The two compounds are crystallographically isomorphous, but each structure was solved and refined independently of the other. The atomic coordinates and equivalent isotropic thermal vibration parameters for **1** and **2** are listed in Tables II and III, respectively. There are 2 molecules in the triclinic unit cell (space group $P\bar{1}$), one residing on the inversion center at (0, 0, 0) and the other on the inversion center at ($^1/_2$, $^1/_2$, $^1/_2$). These two molecules are thus crystallographically nonequivalent, and the crystallographic asymmetric unit is comprised of half of each. One such molecule for compound **2** is shown in the ORTEP diagram in Figure 1, with the atom-labeling scheme. The other molecule in the unit cell is essentially similar to that shown in the figure, and of course, the molecules of compound **1** are analogous and have been labeled in a matching way.

The common structural feature of the two complexes is the presence of four benzamidato ligands bridging the dinuclear osmium(III) centers. In **1** the axial ligand is Cl while in **2** it is Br. The metal centers have essentially octahedral geometry. The average $Os{\equiv}Os$ bond lengths are 2.367 [2] and 2.384 [2] Å in **1** and **2**, respectively. The average Os–Cl and Os–Br bond lengths are 2.490 [9] and 2.611 [5] Å, respectively. The $Os{\equiv}Os$ bond lengths are the longest among $Os_2X_2[L{-}L']_4$ complexes where L–L′ represents a three-atom bridging ligand. Data for the known[2,4-9] complexes of this type are presented in Table V. The Os–Cl distances in **1** are considerably longer than those in carboxylato and ortho-metalated species where they range from 2.37 to 2.45 Å. However, they are equal to or slightly shorter than those found in 2-hydroxypyridine complexes, ca. 2.50 Å.

To date, there is no report available on diosmium species with an axial bromide ion. As expected, the Os–Br bonds are longer than the Os–Cl bonds, but by only about 0.12 Å, whereas the conventional single-bond radii differ by 0.15 Å. A weakening of the Os–Cl bond on going from the carboxylato species to **1** is also apparent from the IR data, as already noted. The X–Os–Os–X chains are not strictly linear, the average Os–Os–X angles being 173.7 [3]° (X = Cl) and 174.1 [2]° (X = Br).

Before the other bond lengths and angles are discussed, it must be pointed out that there exists the possibility of errors greater

Table IV. Some Important Bond Distances (Å) and Angles (deg) in $Os_2Cl_2(PhCONH)_4$ (1) and $Os_2Br_2(PhCONH)_4$ (2)[a,b]

bond dist	Os_2Cl_2-$(PhCONH)_4$	Os_2Br_2-$(PhCONH)_4$	bond dist	Os_2Cl_2 $(PhCONH)_4$	Os_2Br_2-$(PhCONH)_4$
Os(1)-Os(1)	2.369 (2)	2.383 (2)	O(1)-C(11)	1.26 (3)	1.41 (4)
Os(2)-Os(2)	2.365 (3)	2.384 (2)	N(1)-C(11)	1.33 (4)	1.20 (5)
Os(1)-X(1)	2.513 (9)	2.629 (5)	O(2)-C(21)	1.32 (3)	1.24 (5)
Os(2)-X(2)	2.466 (8)	2.592 (5)	N(2)-C(21)	1.28 (3)	1.37 (5)
Os(1)-O(1)	2.04 (2)	2.02 (3)	O(3)-C(31)	1.25 (3)	1.43 (4)
-O(2)	1.95 (2)	2.02 (2)	N(3)-C(31)	1.31 (4)	1.22 (5)
Os(2)-O(3)	2.03 (2)	1.88 (3)	O(4)-C(41)	1.39 (4)	1.36 (5)
-O(4)	2.01 (2)	1.99 (3)	N(4)-C(41)	1.28 (4)	1.32 (4)
Os(1)-N(1)	2.01 (2)	1.98 (3)	C(11)-C(12)	1.51 (5)	1.54 (6)
-N(2)	2.00 (2)	1.96 (3)	C(21)-C(22)	1.58 (4)	1.59 (5)
Os(2)-N(3)	2.04 (2)	1.99 (3)	C(31)-C(32)	1.50 (5)	1.53 (5)
-N(4)	2.02 (2)	2.00 (3)	C(41)-C(42)	1.40 (4)	1.53 (6)

bond angles	Os_2Cl_2-$(PhCONH)_4$	Os_2Br_2-$(PhCONH)_4$	bond angles	Os_2Cl_2-$(PhCONH)_4$	Os_2Br_2-$(PhCONH)_4$
Os(1)-Os(1)-X(1)	175.1 (3)	174.3 (2)	O(1)-Os(1)-O(2)	87.1 (8)	88 (1)
Os(2)-Os(2)-X(2)	172.4 (2)	173.8 (2)	-N(1)	176.7 (8)	176 (1)
Os(1)-Os(1)-O(1)	88.5 (5)	90.3 (7)	-N(2)	93.3 (8)	92 (1)
-O(2)	90.8 (6)	88.4 (7)	O(2)-Os(1)-N(1)	92.7 (9)	90 (1)
-N(1)	88.2 (6)	86.8 (7)	-N(2)	177.6 (9)	177 (1)
-N(2)	86.8 (6)	88.2 (9)	N(1)-Os(1)-N(2)	86.8 (9)	90 (1)
Os(2)-Os(2)-O(3)	89.4 (6)	91.2 (7)	O(3)-Os(2)-O(4)	90.4 (8)	88 (1)
-O(4)	90.3 (6)	91.8 (6)	-N(3)	176.3 (8)	176 (1)
-N(3)	88.4 (7)	85.2 (8)	-N(4)	88.1 (9)	90 (1)
-N(4)	87.5 (7)	87.7 (8)	O(4)-Os(2)-N(3)	86.6 (9)	89 (1)
X(1)-Os(1)-O(1)	90.9 (6)	95.4 (7)	-N(4)	177.4 (9)	178.5 (9)
-O(2)	84.3 (6)	92.0 (7)	N(3)-Os(2)-N(4)	94.8 (9)	92 (1)
-N(1)	92.4 (7)	87.5 (7)	O(1)-C(11)-N(1)	121 (3)	122 (3)
-N(2)	98.1 (7)	91.4 (9)	O(2)-C(21)-N(2)	123 (3)	120 (3)
X(2)-Os(2)-O(3)	89.9 (6)	88.5 (7)	O(3)-C(31)-N(3)	126 (4)	117 (3)
-O(4)	97.2 (7)	94.3 (6)	O(4)-C(31)-N(4)	118 (3)	124 (3)
-N(3)	92.7 (8)	95.3 (8)			
-N(4)	84.9 (7)	86.1 (8)			

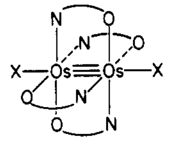
[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] X represents Cl or Br as appropriate.

Table V. Structural and Electrochemical Data of $Os\equiv Os$ Triple-Bonded Complexes

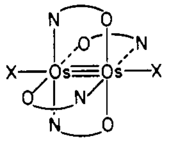
compd	$Os\equiv Os$, Å	Os–Cl, Å	$E_{1/2}$,[a] V (solvent)	ref
$Os_2Cl_2(O_2CCH_3)_4$	2.314 (1)	2.448 (2)		6
$Os_2Cl_2(O_2CEt)_4$	2.316 (2)	2.430 (5)	+0.57 (CH_2Cl_2)	5, 6
$Os_2Cl_2(O_2C\text{-}n\text{-}Pr)_4$	2.301 (1)	2.417 (3)	+0.53 (CH_2Cl_2)	4, 5
$Os_2Cl_2(O_2CCH_3)_2[Ph_2P(C_6H_4)]_2$	2.271 (1)	2.372 (2)		7
$Os_2Cl_2(O_2CEt)_2[Ph_2P(C_6H_4)]_2$	2.272 (1)	2.396 (2)		7
$Os_2Cl_2(NC_5H_4O\text{-}2)_4$	2.357 (1)	2.505 (5)	+0.26 (CH_2Cl_2)	2, 5
$Os_2Cl_2(PhCONH)_4$	2.367 [2]	2.490 [9]	−0.07 (Me_2SO)	this work
$Os_2Cl_3(PhNpy)_3$	2.392 (1)	2.376 [5]	−0.23 (CH_2Cl_2)	8

[a] Formal potential of the couple $[Os^{III}Os^{III}] + e^- \rightarrow [Os^{III}Os^{II}]^-$.

than those given by the routine calculation of estimated standard deviations (esd's). This is because there is disorder in the arrangement of the benzamidato bridging ligands, and we have not devised a model that fits precisely. There are four possible arrangements within any one molecule, shown as II–V. The crystallographic symmetry requires only that whatever subset or mixture of these is present, in whatever porportions, they be arranged so as to give an average distribution of electron density that is centrosymmetric for each molecular position. We have assumed (with some confidence) that IV and V need not be considered. We have also, somewhat more arbitrarily, assumed that II, the only inherently centrosymmetric structure, is more probable than III, and far more probable than a mixture of II and III. We then used a twofold disordered set of molecules of type II and adjusted the ratios of the two orientations at each site so as to give the most reasonable thermal vibration parameters consistent with also having low discrepancy indices. However, there are imperfections in the final model. Lower discrepancy indices could be achieved by relaxing constraints based on the thermal parameters, while more equal thermal parameters for pairs of N and O atoms could be achieved at the expense of higher discrepancy indices. Since nothing of chemical importance could be obtained by further efforts, we have terminated the refinement at the discrepancy indices given in Table I, without attempting to refine a more complicated model.



II



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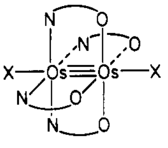

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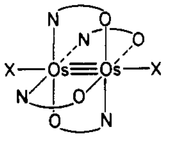

V

The various bond lengths and angles involving N and O atoms are not as precisely defined as would ordinarily be the case because of the disorder problem just discussed. We therefore do not believe that they merit discussion beyond noting that the ranges in which they occur are quite reasonable. The Os–Os–O and Os–Os–N angles lie in the range 88.4 (7)–91.8 (6)° and 85.2 (8)–88.4 (7)°, respectively. The O–C–N angles lie in the range 117 (3) and 126 (4)°. The Os–O and Os–N bond lengths are in the ranges 1.88 (3)–2.04 (2) and 1.96 (3)–2.04 (2) Å, respectively. The torsion

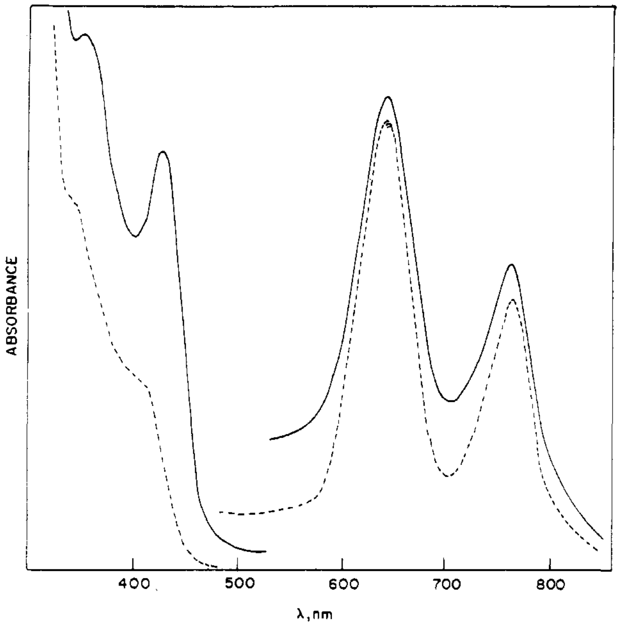

Figure 2. Electronic spectra of $Os_2Br_2(PhCONH)_4$ (—) and $Os_2Cl_2(PhCONH)_4$ (---) in CH_2Cl_2. Molar extinction coefficients of the band maxima are given in the Experimental Section.

angles, O–Os–Os–N, are in the range 1.0–2.9°.

Electronic Spectra. In Me_2SO, both compounds exhibit bands at 635 and 750 nm. In CH_2Cl_2, the bands are at 643 and 762 nm. In addition, the dichloro species exhibits two shoulders at 410 and 345 nm, and the dibromo analogue shows two bands at 427 and 350 nm. The spectra of the complexes are shown in the Figure 2.

The lowest energy bands reported[5] for $Os_2Cl_2(hp)_4$ and $Os_2Cl_2(O_2CR)_4$ are at 488 and 392 nm, respectively. The electronic spectrum of the asymmetric compound $Os_2Cl_3(PhNpy)_3$ is known[8] to have two distinct low-energy absorptions at 868 and 615 nm along with two shoulders at 527 and 455 nm. An interpretation of these spectra, which is made unusually difficult because of the spin state equilibrium, must await further work. A study of the temperature dependence will be particularly helpful.

Electrochemistry. The electrochemical behavior of $Os_2Cl_2(PhCONH)_4$ was studied by cyclic voltammetry in Me_2SO in the presence of 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte at 298 K. The compound undergoes a one-electron reduction at −0.07 V vs. SCE. The peak-to-peak separation is 140 mV at a scan rate of 20 mV s^{-1}. The electron-transfer process is thus quasi-reversible. The anodic to cathodic peak current ratio is 1.0, and the peak currents remain constant on repeated scans. In addition, the compound exhibits an irreversible oxidation at +1.37 V. No more reductions were observed in scans out to a limit of −2.0 V. The reduction of −0.07 V is believed to be due to the formation of the mixed-valence species $[Os_2Cl_2(PhCONH)_4]^-$.

Except for the ortho-metalated compounds, $Os_2Cl_2(O_2CR)_2[Ph_2P(C_6H_4)]_2$,[7] which are diamagnetic, all other previously known[5,8] diosmium compounds have been paramagnetic. It is believed that these paramagnetic species have a singlet ground state derived from the configuration $\sigma^2\pi^4\delta^2\delta^{*2}$ as well as a considerably populated triplet state derived from configurations such as $\sigma^2\pi^4\delta^2\pi^{*2}$ or $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*1}$. In the reduction of the diosmium compounds, the addition of one electron is expected to give either or both of the configurations $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*1}$ or $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*1}$. Comparison of the formal reduction potentials of known diosmium compounds (Table V) shows that the $E_{1/2}$ values and the Os≡Os bond lengths are sensitive to the nature of the bridging ligands. An increase in the formal reduction potential follows the order of decreasing Os≡Os triple-bond lengths, and there is an approximately linear correlation between the formal reduction potentials and the Os≡Os triple-bond lengths, as shown in Figure 3. From electrochemical studies we get a qualitative order of ligands in stabilizing the higher oxidation state. Among $Os_2Cl_2(L\text{–}L')_4$, the order of L–L′ is $[(C_6H_4)PPh_2]^-$ > $(RCOO)^-$ > hp^- > $[PhCONH]^-$. This is in accord with the known fact[12–14] that among diruthenium complexes of the type $Ru_2(L\text{–}L')_4Cl$ amides are better stabilizers of the higher oxidation state than carboxylates.

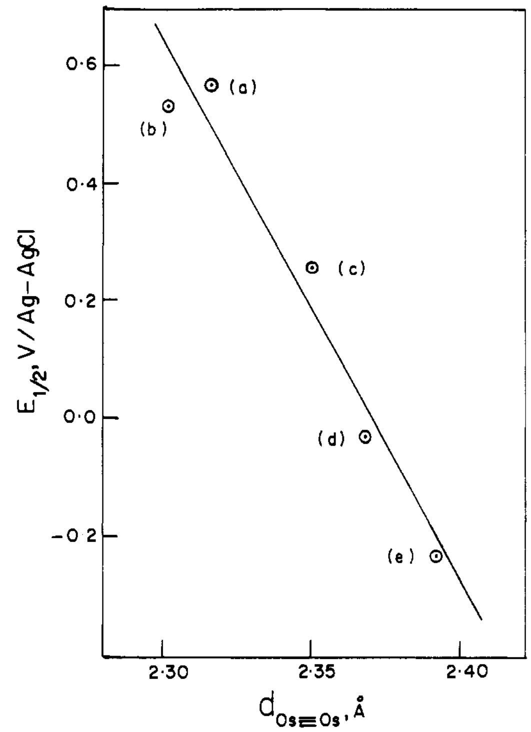

Figure 3. Linear correlation between formal reduction potentials and Os≡Os triple-bond lengths. Compounds: (a) $Os_2Cl_2(O_2CEt)_4$;[5,6] (b) $Os_2Cl_2(O_2C\text{-}n\text{-}Pr)_4$;[4,5] (c) $Os_2Cl_2(NC_5H_4O\text{-}2)_4$;[2,5] (d) $Os_2Cl_2(PhCONH)_4$; (e) $Os_2Cl_3(PhNpy)_3$.[8]

Acknowledgment. We are grateful to the National Science Foundation for financial support and to Dr. B. B. Hutchinson for the magnetic susceptibility measurement.

Registry No. **1**, 93121-30-3; **2**, 95482-46-5; $Os_2Cl_2(O_2CCH_3)_4$, 81519-41-7; Os, 7440-04-2.

Supplementary Material Available: Listings of structure factors, anisotropic thermal parameters, and bond distances and bond angles and a description of the crystal structure determination (45 pages). Ordering information is given on any current masthead page.

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(15) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)