with experiment. For a given ring position, the SE's increase in the order $NH_2 < OH < F$ as expected on the basis of both the unfavorable π-donating ($NH_2 > OH > F$) and favorable σ-accepting ($NH_2 < OH < F$) properties of this set of substituents. For a given substituent, the SE's increase in the order *para* < *ortho* < *meta*. Furthermore, the difference in SE's for *ortho* and *para* substitution increases in the order F < OH < NH_2. These results are all consistent with observed rate data.[10] Calculations on the fluoro-substituted system have recently been reported[15] which also predict a stability order of *para* < *ortho* < *meta*.

The results for methyl group are least satisfactory when compared with experiment. This is not unexpected with such a weakly perturbing substituent since other factors such as solvation, leaving group, and nucleophile can be expected to play a more dominant role in determining the rate of reaction.

Conclusions

(1) The equilibrium structure of the cyclohexadienyl anion has a planar ring, and is therefore nonhomoaromatic at the STO-3G level. This agrees with most experimental and previous theoretical data. The homocyclopentadienyl anion is nevertheless predicted to correspond to a local minimum in the $C_6H_7^-$ energy surface.

(2) The relative isomer energies and stabilization energies of 1-, 2- and 3-substituted cyclohexadienyl anions are ordered in accordance with the coefficients of the highest occupied molecular orbital of CHD^-. Greatest stabilization for the π acceptors, or destabilization for the π donors, occurs when the substituent is attached to C(3) (i.e., *para* to the methylene group), and least stabilization/destabilization occurs at C(1). 6-Substituted isomers are stabilized by σ-electron-withdrawing substituents.

(3) Molecular electrostatic potential plots of substituted cyclohexadienyl anions predict that kinetic protonation takes place preferentially at the carbon atom *para* to the first protonation site (i.e., at C(3)). This is so regardless of substituent or of substituent position. Protonation can occur at the *ortho* carbons also, but at a slower rate. When a π donor is substituted at C(1), or a π acceptor at C(2), protonation at the C(1) carbon is impeded.

(4) Rates of nucleophilic substitution reactions of substituted benzenes correlate well with the calculated stabilities (relative to corresponding substituted benzenes) of the substituted cyclohexadienyl anion intermediates involved in the addition/elimination mechanism.

A Triple Bond between Osmium Atoms. Preparation and Structure of Dichlorotetrakis(2-hydroxypyridinato)diosmium(III)

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Abstract: The reaction of osmium(III) chloride with 2-hydroxypyridine (α-pyridone) in ethanol gives the dark red to red-purple $Os_2(hp)_4Cl_2$, where hp = 2-hydroxypyridine anion. This air-stable substance has been obtained in crystalline form as the monoetherate, **1**, and as the bisacetonitrile solvate, **2**, and X-ray crystal structure analysis has been performed on both. **1** forms orthorhombic crystals with $a = 10.036$ (1) Å, $b = 12.114$ (1) Å, and $c = 11.003$ (1) Å, and refinement to $R_1 = 0.037$ and $R_2 = 0.047$ was carried out in space group *Pmmn* by using a disordered model, based on molecules of D_2 symmetry with an internal twist angle of 17.5°. **2** forms monoclinic crystals with $a = 9.416$ (1) Å, $b = 17.304(3)$ Å, $c = 17.331$ (2) Å, $\beta = 90.70$ (1)°, and refinement in space group $P2_1/n$ was convergent with $R_1 = 0.040$ and $R_2 = 0.043$. In this compound also the virtual molecular symmetry was D_2 but the twist angle was 5.5°. The Os-Os distances were 2.344 (2) and 2.357 (1) Å in **1** and **2**, respectively. The difference in twist angles is presumably caused by different intermolecular forces.

Introduction

In the developing chemistry of compounds containing multiple bonds between atoms of the transition metals[1,2] the discovery of entirely new M-M multiple bonds is still possible and is, indeed, one of the most important goals. In view of the extensive chemistry of both triple and quadruple bonds between rhenium atoms and the existence of some multiple bonds between ruthenium atoms[3] we considered osmium an excellent candidate for the formation of new multiple M-M bonds. Our thinking took the following concrete form, leading rationally to the results reported here.

While the electronic population would be right for the existence of a quadruple bond between two Os^{IV} ions, it has long been recognized[4] that M-M bonds, especially multiple ones, are favored by lower oxidation numbers and indeed no triple or quadruple bond is yet known between metal atoms in oxidation states as high as +4. Hence, we turned our attention to the possibility of an $Os^{III}\equiv Os^{III}$ triple bond. This would have to be of the same electronic type as those between Re^{II} atoms, where the central electron configuration is formally $\sigma^2\pi^4\delta^2\delta^{*2}$. The bond order of 3 is due to the six electrons occupying the σ and π orbitals, since the δ bonding is cancelled by the presence of two δ^* electrons. Since many triple bonds of the simple $\sigma^2\pi^4$ type exist between M^{III} atoms,[2] including the recently described $[Mo_2(HPO_4)_4]^{2-}$ species,[5] a compound containing an $Os^{III}\equiv Os^{III}$ bond seemed a plausible objective.

The question of what ligands to use admitted of several viable answers. A set of three-atom bridging ligands seemed most attractive and of the various possibilities[6] we selected the 2-hydroxypyridine anion, hp, as an initial candidate. Considering then the recent isolation and structural characterization[7] of

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(1) Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225.
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(3) Bino, A.; Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1979**, *18*, 2599.
(4) Cotton, F. A. *Acc. Chem. Res.* **1969**, *2*, 240.
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(6) Cotton, F. A.; Rice, G. W.; Sekutowski, J. C. *Inorg. Chem.* **1979**, *18*, 1143.
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$Re_2(hp)_4Cl_2$, we focused on $Os_2(hp)_4Cl_2$ as our specific objective. In this paper we describe the preparation and structure of this molecule, the first compound known that contains a multiple bond between osmium atoms.

Experimental Section

Preparation. A mixture of 100 mL of absolute ethanol, 1.0 g of 2-hydroxypyridine (α-pyridone) and 0.50 g of osmium(III) chloride was refluxed under nitrogen. Over a period of 12 h the color of the reaction mixture changed from brown to dark red. The solvent was removed by vacuum distillation and the resulting dark residue extracted several times with CH_2Cl_2. Evaporation of this solution produced a microcrystalline, air-stable product, which had an elemental analysis approximating to $Os_2(hp)_4Cl_2 \cdot 2CH_2Cl_2$. Yield: 1.06 g, 72%. This substance is soluble in most common solvents, e.g., tetrahydrofuran, ethyl ether, and acetonitrile. Recrystallization from acetonitrile gave a microcrystalline sample of what appears to be $Os_2(hp)_4Cl_2 \cdot CH_2Cl_2 \cdot CH_3CN$. Anal. Calcd: C, 29.00; H, 2.20; N, 7.34; Cl, 14.88. Found: C, 30.9; H, 2.76; N, 7.42; Cl, 14.4. No crystals suitable for X-ray work were obtained in this way.

By slow evaporation of a solution in CH_2Cl_2/Et_2O, approximately 1:1, crystallographically useful crystals of $Os_2(hp)_4Cl_2 \cdot Et_2O$ (**1**), were obtained. When a sample of **1** was dissolved in acetonitrile and this solution slowly evaporated, crystals of $Os_2(hp)_4Cl_2 \cdot 2CH_3CN$ (**2**) were obtained.

X-ray Study of 1. A dark purple crystal with approximate dimensions of 0.10 × 0.12 × 0.15 mm was attached with epoxy cement to a glass fiber and mounted on an Enraf-Nonius CAD-4F automated diffractometer. Procedures used to collect and process data for this compound and also for **2** were essentially the same as those reported before.[8] Indexing on 25 intense centered reflections in the range $25° \leq 2\theta \leq 45°$, a unit cell in the orthorhombic system was defined with the following dimensions: $a = 10.036$ (1) Å, $b = 12.114$ (1) Å, $c = 11.003$ (1) Å, and $V = 1338$ (1) Å^3. This volume is consistent with $Z = 2$. Systematic absences of $hk0$ with $h + k \neq 2n$ were observed, indicating space groups $Pmmn$ (No. 59) or $Pmn2_1$ (No. 31).

Data were collected in the usual way.[8] The linear absorption coefficient of 103 cm^{-1} made an absorption correction necessary. An empirical method was used in which a ψ scan for each of seven reflections was made near $\chi = 90°$. Each reflection was measured at 10° intervals from $\psi = 0°$ to $\psi = 360°$. The normalized transmission factors obtained varied from 1.00 to 0.73. With use of Mo Kα radiation ($\lambda = 0.71073$ Å), 1037 reflections were collected in the range of $0° < 2\theta \leq 45°$; the 651 reflections having $I > 3\sigma(I)$ were used to solve and refine the structure.

Statistical tests indicated the space group to be the centric one, $Pmmn$. The positions of the two Os atoms were located by the direct methods program MULTAN.[9] Refinement of these positions gave discrepancy indices of

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.16$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.20$$

A difference Fourier map indicated that the independent ligand of the asymmetric unit was disordered. Location of the remaining 21 atoms by refinement and difference Fourier maps confirmed the disorder. Attempts to eliminate the disorder of the ligand by refinement in the acentric space group $Pmn2_1$ produced a model that was physically infeasible. Returning to the space group $Pmmn$, refinement was completed.

The model refined is as follows. The Os and Cl atoms are perfectly ordered; all of them occupy the twofold a positions of $Pmmn$ with the origin at $\bar{1}$. Thus, there are Cl-Os-Os-Cl chains lying on the twofold axes at the intersection of the two crystallographic mirror planes at $^1/_4$, $^1/_4$, z and $^3/_4$, $^3/_4$, z. The bidentate bridging ligands are arranged around these in a disordered fashion. Around Os(1) are placed only four discrete atoms at bonding distance, and each one is refined as $^1/_2$N + $^1/_2$O while around Os(2) eight discrete atoms are placed at bonding distances, four of which are refined as $^1/_2$N and the other four as $^1/_2$O. All the remaining ring atoms of the ligands are refined as ten $^1/_2$C atoms. This corresponds stereochemically to the placement of two enantiomorphous twisted molecules, each with half-weight at each molecular position. Each molecule has D_2 symmetry, which means that on each metal atom we have N trans to N (and, of course, O trans to O). On Os(1) half the molecules have one of the two possible arrangements of the N and O atoms and twist clockwise while the other half have the alternate arrangement of the N and O atoms and twist counterclockwise. This produces a total configuration made up of the two half molecules that satisifies the required crystallographic C_{2v} symmetry.

No arrangment of molecules with a *cis*-N_2O_2 ligand set at each metal atom will suffice in either space group nor can any arrangement of D_2 molecules suffice in space group $Pmn2_1$. We ruled out the possibility of using molecules with all of the N atoms on one Os atom for chemical reasons, although a disordered arrangement of such species would not be inconsistent with the crystallographic symmetry. Note that for compound **2** where no disorder problem occurs the molecules have D_2 symmetry.

With use of anisotropic thermal parameters for the Os, Cl, N, and O atoms and isotropic ones for the ligand carbon atoms and the atoms in the ether molecule, refinement converged with $R_1 = 0.037$, $R_2 = 0.047$, and the esd in an observation of unit weight equal to 1.19. The final difference map was clean except for a few weak peaks very close to the osmium atoms and a few weak peaks that were approximately where some of the hydrogen atoms might have been expected. In view of the small data set and the disorder, no consideration was given to the refinement of hydrogen atoms.

X-ray Study of 2. A dark red crystal of approximate dimensions 0.10 × 0.10 × 0.15 mm was attached to a glass fiber with epoxy cement mounted on the CAD-4F diffractometer. Indexing on 25 intense reflections in the range $25° \leq 2\theta \leq 45°$ produced a unit cell in the monoclinic system with dimensions $a = 9.416$ (1) Å, $b = 17.304$ (3) Å, $c = 17.331$ (2) Å, and $\beta = 90.70$ (1)°, with $V = 2823$ (1) Å^3. The observed volume is consistent with $Z = 4$. Systematic absences of $h0l$, $h + l \neq 2n$, and $0k0$, $k \neq 2n$, were observed, indicating the space group as $P2_1/n$.

A total of 5162 reflections between $0° < 2\theta \leq 50°$ was collected as previously described, and those 2351 having $I \geq 3\sigma(I)$ were used in solving and refining the structure. Three reflections checked every hour for decay in intensity showed a linear decay of 15%, and a correction was made. The linear absorption coefficient of 97.9 required that an absorption correction be made. Nine reflections were treated as previously described, the normalized transmission factors ranging from 1.00 to 0.70.

The approximate positions of the two Os atoms were obtained from a three-dimensional Patterson map. Initial refinement gave discrepancy indices of $R_1 = 0.17$ and $R_2 = 0.23$. The remaining 36 atoms were located by subsequent refinement and difference Fourier maps. Final refinement on the positional and anisotropic thermal parameters for all atoms gave $R_1 = 0.040$ and $R_2 = 0.043$. The estimated standard deviation of an observation of unit weight after the final least-squares cycle was 0.99. A final difference map revealed peaks probably associated with hydrogen atoms, but we did not consider it worthwhile to continue refinement including them.

Results and Discussion

The preparation of $Os_2(hp)_4Cl_2$ is straightforward and the compound itself has benchtop stability, indefinitely, under normal conditions. Hence, once again, we find that the chemistry of M-M multiple bonds is neither exotic nor difficult–only neglected. We shall now discuss each of the two new compounds in detail.

$Os_2(hp)_4Cl_2 \cdot (C_2H_5)_2O$ (1). This crystalline compound was isolated and studied first, and it was because of the severe difficulties that arose from the disordered crystal packing that we proceeded to compound **2**. The disorder model we refined and the reasons for the choice of this model in space group $Pmmn$ have been explained in the Experimental Section. There is, of course, always an element of uncertainty for disordered models that is not present in the routine structure refinements. We believe, however, that the very good figures of merit obtained (admittedly helped by the relatively small data set) plus the absence of any abnormalities of either a chemical nature (e.g., unusual bond lengths) or a crystallographic nature (e.g., unreasonable thermal parameters (except for B_{33} of Cl(1)); significant peaks in the final difference map) give adequate grounds for accepting that our model is essentially correct and that the picture of the molecule (Figure 1) so obtained is correct.

The positional and thermal parameters are listed in Table I and the bond lengths and bond angles in Tables II and III. The atom numbering scheme used in these tables is defined in Figure 1. The molecule has the ligands arranged with like atoms trans on each metal atom. This arrangement would lead to D_{2d} symmetry were it not for the fact that the ligands are all tilted in a concerted way to give the molecule a helical twist and reduce the symmetry to D_2. The twist angle is 17.5°.

It is notable that the disorder in this structure can be viewed as having two components, each of which is already known to occur

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[8] Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

[9] All computing to solve and refine the structures was carried out on a PDP 11/45 computer at the Molecular Structure Corporation, College Station, Texas, using the ENRAF-NONIUS structure determination package with some local modifications.

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for Compound 1

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	0.7500 (0)	0.7500 (0)	0.18766 (9)	2.83 (5)	2.37 (5)	2.29 (4)	0	0	0
Os(2)	0.7500 (0)	0.7500 (0)	0.40074 (9)	3.16 (5)	2.11 (5)	1.58 (4)	0	0	0
Cl(1)	0.7500 (0)	0.7500 (0)	−0.0392 (5)	5.9 (4)	4.6 (3)	0.4 (2)	0	0	0
Cl(2)	0.7500 (0)	0.7500 (0)	0.6253 (8)	4.5 (4)	5.8 (4)	4.7 (4)	0	0	0
O(1)	0.653 (2)	0.608 (1)	0.403 (1)	3.2 (8)	3.1 (8)	2.5 (7)	−0.2 (8)	−0.2 (6)	0.5 (6)
O(2)	0.606 (0)	0.637 (0)	0.190 (0)	7	11	2	−6	0	−2
O(3)	0.7500 (0)	0.2500 (0)	0.228 (4)	14 (1)					
N(1)	0.606 (3)	0.637 (3)	0.190 (2)	8 (2)	12 (2)	3 (1)	−6 (2)	1 (1)	−2 (1)
N(2)	0.563 (2)	0.676 (2)	0.393 (2)	2.0 (9)	5 (1)	1.6 (7)	−0.6 (9)	0.2 (8)	1.0 (9)

atom	x	y	z	B_{11}	atom	x	y	z	B_{11}
C(11)	0.605 (3)	0.563 (2)	0.301 (2)	3.0 (5)	C(22)	0.396 (3)	0.582 (3)	0.279 (3)	5.0 (7)
C(12)	0.520 (4)	0.473 (3)	0.312 (3)	4.9 (7)	C(23)	0.317 (3)	0.562 (3)	0.376 (3)	6.7 (9)
C(13)	0.461 (3)	0.422 (3)	0.211 (3)	5.0 (7)	C(24)	0.365 (3)	0.609 (3)	0.484 (3)	6.5 (9)
C(14)	0.487 (3)	0.472 (2)	0.098 (2)	3.8 (6)	C(25)	0.484 (3)	0.659 (2)	0.496 (3)	4.6 (7)
C(15)	0.576 (3)	0.562 (2)	0.093 (2)	3.5 (6)	C(31)	0.661 (5)	0.331 (5)	0.148 (4)	13.2 (18)
C(21)	0.519 (3)	0.634 (2)	0.285 (2)	3.1 (5)	C(32)	0.699 (5)	0.250 (0)	0.030 (4)	18.8 (18)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table II. Bond Distances (Å) in $Os_2(hp)_4Cl_2\cdot(CH_3CH_2)_2O$ (1)

Os(1)–Os(2)	2.344 (2)	C(21)–N(2)	1.36 (3)
Cl(1)	2.496 (7)	O(2)	1.36 (3)
N(1)	1.99 (3)	C(22)	1.39 (4)
O(2)	1.99 (3)	C(25)–N(2)	1.40 (3)
Os(2)–Cl(2)	2.47 (1)	C(24)	1.35 (4)
N(2)	2.08 (2)	C(23)–C(22)	1.34 (4)
O(1)	1.98 (2)	C(24)	1.40 (4)
C(11)–N(1)	1.52 (4)	C(31)–O(3)	1.60 (6)
O(1)	1.33 (3)	C(32)	1.67 (6)
C(12)	1.38 (4)		
C(15)–N(1)	1.44 (4)		
C(14)	1.41 (4)		
C(13)–C(12)	1.40 (4)		
C(14)	1.40 (4)		

Table III. Bond Angles (Deg) in $Os_2(hp)_4Cl_2\cdot(CH_3CH_2)_2O$ (1)

Os(1)–Os(2)–Cl(2)	180	Os(2)–Os(1)–Cl(1)	180
N(2)	87.7 (5)	N(1)	89.10 (4)
O(1)	90.7 (4)	O(2)	89.10 (4)
N(1)–Os(1)–Cl(1)	90.90 (4)	N(2)–Os(2)–Cl(2)	92.3 (5)
N(1)′	178.20 (7)	N(2)′	175 (1)
O(2)	93.16 (7)	O(1)	94 (1)
O(2)′	86.81 (7)	O(1)′	86 (1)
N(1)–C(11)–O(1)	115 (2)	N(2)–C(21)–O(2)	116 (2)
C(12)	123 (2)	C(22)	120 (3)
N(1)–C(15)–C(14)	126 (3)	N(2)–C(25)–C(24)	119 (3)
O(2)–Os(1)–Cl(1)	90.90 (4)	O(1)–Os(2)–Cl(2)	89.3 (4)
O(2)′	178.20 (7)	O(1)′	178.6 (8)
O(2)–C(21)–C(22)	12.3 (2)	O(1)–C(11)–C(22)	118 (2)
C(11)–N(1)–C(15)	103 (3)	C(21)–N(2)–C(25)	118 (2)
C(12)–C(13)	122 (3)	C(22)–C(23)	124 (3)
C(12)–C(13)–C(14)	116 (3)	C(22)–C(23)–C(24)	114 (3)
C(13)–C(14)–C(15)	119 (3)	C(23)–C(24)–C(25)	125 (3)
		O(3)–C(31)–C(32)	86 (4)
		C(31)–O(3)–C(31)′	112 (6)

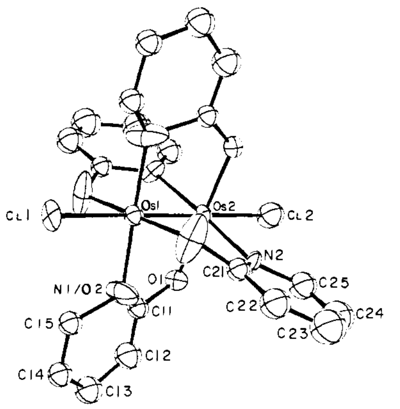

Figure 1. An ORTEP drawing of the $Os_2(hp)_4Cl_2$ molecule as it is found in the etherate, compound **1**. The other enantiomorph also occurs in the crystal. Each atom is represented by its ellipsoid of thermal vibration, scaled to enclose 30% of the electron density.

in related structures. First, we have the disordering of the two enantiomeric "twistomers". This has previously been seen[10] in the compound $Mo_2[PF_2N(CH_3)PF_2)]_4Cl_2$. Second, we have the "up–down" disordering of unsymmetrical bridging ligands. This has been seen quite often before.[11,12] This is the first time both of these forms of disorder have been seen together at the same crystal site.

$Os_2(hp)_4Cl_2\cdot 2CH_3CN$ (2). This compound presented no unusual problems in the solution and refinement of the crystal structure. The space group is $P2_1/n$, and with $Z = 4$ the entire molecule is the asymmetric unit. The positional and thermal parameters are listed in Table IV, and the bond lengths and bond angles are presented in Tables V and VI. The molecule is depicted in Figure 2 where the atom numbering scheme is defined.

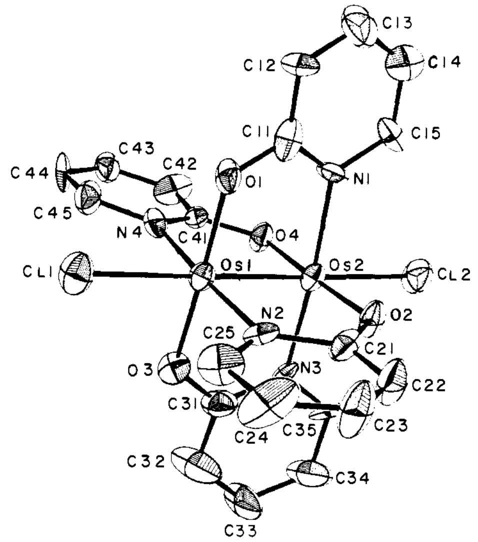

Figure 2. One enantiomorph of the $Os_2(hp)_4Cl_2$ molecule as it is found in the acetonitrile solvate, **2**. Thermal ellipsoids are scaled to enclose 30% of the electron density of each atom.

The structure has D_{2d} symmetry, thus supporting the model refined in the case of compound **1**. However, the degree of twist

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[10] Cotton, F. A.; Ilsley, W. H.; Kaim, W. *J. Am. Chem. Soc.* **1980**, *102*, 1918.

[11] Cotton, F. A.; Gage, L. D. *Inorg. Chem.* **1979**, *18*, 1716.

[12] Cotton, F. A.; Fanwick, P. E.; Gage, L. D. *J. Am. Chem. Soc.* **1980**, *102*, 1570.

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for Compound 2

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	0.26715 (8)	0.10828 (4)	0.16369 (4)	2.33 (3)	1.66 (2)	2.04 (2)	0.12 (3)	0.26 (2)	−0.12 (3)
Os(2)	0.11596 (8)	0.21014 (4)	0.20020 (4)	2.38 (3)	1.81 (2)	1.87 (2)	0.18 (3)	0.32 (2)	−0.26 (3)
Cl(1)	0.4224 (5)	−0.0023 (3)	0.1248 (3)	4.3 (2)	2.4 (2)	3.8 (2)	0.9 (2)	0.6 (2)	0.1 (2)
Cl(2)	−0.0411 (5)	0.3214 (3)	0.2335 (3)	4.0 (2)	3.3 (2)	3.3 (2)	1.2 (2)	0.3 (2)	−0.9 (2)
O(1)	0.104 (1)	0.0534 (6)	0.1136 (6)	2.3 (5)	1.8 (5)	3.4 (5)	0.4 (4)	0.7 (4)	−0.6 (4)
O(2)	0.060 (1)	0.1549 (6)	0.2937 (6)	3.8 (6)	3.3 (5)	1.6 (4)	1.5 (5)	0.9 (4)	0.9 (4)
O(3)	0.431 (1)	0.1603 (6)	0.2107 (6)	3.1 (6)	1.7 (5)	3.3 (5)	−0.2 (4)	0.0 (5)	−0.4 (4)
O(4)	0.166 (1)	0.2669 (6)	0.1056 (6)	2.8 (5)	2.5 (5)	1.8 (4)	1.0 (4)	0.5 (4)	−0.1 (4)
N(1)	−0.045 (1)	0.1540 (8)	0.1371 (7)	1.4 (6)	3.5 (7)	2.4 (6)	−0.4 (6)	−0.9 (5)	0.1 (6)
N(2)	0.223 (1)	0.0565 (8)	0.2702 (7)	2.9 (7)	4.1 (7)	1.6 (6)	−0.2 (6)	−0.6 (5)	−0.9 (6)
N(3)	0.287 (1)	0.2567 (7)	0.2586 (7)	3.5 (7)	1.2 (5)	1.5 (5)	0.2 (5)	0.3 (5)	−0.6 (5)
N(4)	0.300 (1)	0.1662 (7)	0.0579 (7)	1.6 (6)	2.3 (6)	2.8 (6)	−0.1 (5)	0.5 (5)	0.1 (5)
N(111)	0.128 (3)	0.1483 (16)	0.5666 (17)	11 (2)	13 (2)	14 (2)	−3 (2)	−4 (2)	−2 (2)
N(211)	0.656 (3)	0.0546 (18)	0.3889 (17)	13 (2)	17 (2)	12 (2)	−6 (2)	3 (2)	−3 (2)
C(11)	−0.022 (2)	0.0833 (9)	0.1066 (10)	4.1 (9)	1.9 (7)	3.0 (8)	0.3 (7)	1.7 (7)	0.5 (6)
C(12)	−0.128 (2)	0.0459 (11)	0.0634 (10)	2.5 (8)	4.4 (9)	3.1 (8)	−0.9 (8)	−0.9 (7)	−1.0 (8)
C(13)	−0.257 (2)	0.0786 (12)	0.0537 (13)	2.8 (9)	5 (1)	8 (1)	−1.3 (9)	1.1 (9)	−2 (1)
C(14)	−0.283 (2)	0.1493 (13)	0.0861 (12)	4 (1)	6 (1)	5 (1)	0 (1)	−0.3 (9)	−2 (1)
C(15)	−0.179 (2)	0.1865 (11)	0.1289 (11)	1.4 (7)	5 (1)	4.4 (9)	0.3 (7)	0.1 (7)	−0.2 (8)
C(21)	0.118 (2)	0.0908 (10)	0.3189 (9)	3.5 (9)	2.9 (8)	2.0 (7)	−0.2 (7)	0.3 (7)	−0.8 (6)
C(22)	0.079 (2)	0.0542 (11)	0.3871 (10)	5 (1)	5 (1)	2.8 (8)	0.8 (9)	1.7 (7)	0.4 (8)
C(23)	0.144 (2)	−0.0138 (11)	0.4063 (11)	7 (1)	4 (1)	3.2 (8)	1.6 (9)	2.6 (8)	1.5 (8)
C(24)	0.252 (3)	−0.0448 (11)	0.3624 (11)	10 (2)	2.8 (9)	2.9 (9)	1 (1)	0 (1)	1.4 (7)
C(25)	0.293 (2)	−0.0090 (10)	0.2938 (11)	5 (1)	2.3 (8)	3.9 (9)	0.2 (8)	−0.4 (8)	1.1 (7)
C(31)	0.419 (2)	0.2238 (10)	0.2521 (10)	3.0 (9)	3.2 (9)	3.2 (8)	−0.5 (7)	−0.7 (7)	−0.6 (7)
C(32)	0.542 (2)	0.2571 (13)	0.2859 (15)	4 (1)	5 (1)	9 (2)	1 (1)	−3 (1)	−1 (1)
C(33)	0.530 (2)	0.3233 (12)	0.3338 (13)	4 (1)	5 (1)	8 (1)	2.9 (9)	−2 (1)	−3 (1)
C(34)	0.391 (2)	0.3538 (13)	0.3429 (12)	5 (1)	5 (1)	5 (1)	1 (1)	−2.6 (9)	−1 (1)
C(35)	0.272 (2)	0.3232 (10)	0.3043 (9)	5 (1)	3.4 (8)	1.2 (6)	0.1 (8)	−1.8 (7)	−0.5 (7)
C(41)	0.245 (2)	0.2390 (9)	0.0505 (9)	1.7 (7)	2.7 (7)	2.5 (7)	−0.2 (6)	−0.1 (6)	−1.5 (6)
C(42)	0.264 (2)	0.2847 (10)	−0.0156 (10)	5 (1)	3.0 (8)	2.5 (7)	−1.6 (8)	0.2 (7)	0.8 (7)
C(43)	0.346 (2)	0.2518 (10)	−0.0744 (11)	2.1 (8)	3.4 (8)	4.5 (9)	−0.6 (7)	0.7 (7)	−1.7 (8)
C(44)	0.404 (2)	0.1758 (11)	−0.0648 (10)	1.8 (7)	5 (1)	3.4 (8)	0.3 (7)	2.3 (6)	−0.2 (8)
C(45)	0.375 (2)	0.1349 (10)	−0.0012 (10)	2.6 (8)	3.5 (9)	3.0 (8)	−0.4 (7)	1.0 (7)	−0.5 (7)
C(111)	0.245 (3)	0.1401 (17)	0.5423 (18)	9 (2)	9 (2)	11 (2)	−4 (1)	−5 (1)	−3 (2)
C(112)	0.385 (4)	0.1365 (23)	0.5085 (25)	10 (2)	18 (3)	20 (3)	−8 (2)	7 (2)	−7 (3)
C(211)	0.700 (3)	0.0353 (16)	0.3322 (18)	10 (2)	7 (2)	11 (2)	−2 (2)	−1 (2)	1 (2)
C(212)	0.741 (4)	0.0010 (21)	0.2632 (15)	14 (2)	15 (3)	5 (1)	−4 (2)	2 (1)	−0 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table V. Bond Distances (Å) in $Os_2(hp)_4Cl_2 \cdot 2CH_3CN$ (2)

Os(1)–Os(2)	2.357 (1)	C(21)–O(2)	1.31 (2)
Cl(1)	2.505 (5)	N(2)	1.44 (2)
O(1)	1.99 (1)	C(22)	1.39 (2)
O(3)	1.95 (1)	C(25)–N(2)	1.37 (2)
N(2)	2.10 (2)	C(24)	1.40 (3)
N(4)	2.12 (1)	C(23)–C(22)	1.36 (3)
Os(2)–Cl(2)	2.500 (5)	C(24)	1.39 (3)
O(2)	1.96 (1)	C(31)–O(3)	1.32 (2)
O(4)	1.97 (1)	N(3)	1.37 (2)
N(1)	2.10 (1)	C(32)	1.41 (3)
N(3)	2.06 (1)	C(35)–N(3)	1.41 (2)
C(11)–O(1)	1.30 (2)	C(34)	1.40 (3)
N(1)	1.35 (2)	C(33)–C(32)	1.42 (3)
C(12)	1.40 (3)	C(34)	1.42 (3)
C(15)–N(1)	1.39 (2)	C(41)–O(4)	1.31 (2)
C(14)	1.38 (3)	N(4)	1.37 (2)
C(13)–C(12)	1.35 (3)	C(42)	1.40 (2)
C(14)	1.37 (3)	C(45)–N(4)	1.36 (2)
C(111)–N(111)	1.19 (5)	C(44)	1.34 (3)
C(112)	1.45 (5)	C(43)–C(42)	1.41 (2)
C(211)–N(211)	1.12 (4)	C(44)	1.43 (3)
C(212)	1.40 (5)		

is significantly different. There are four independent torsion angles, as listed in Table VII, which have an average value of 5.5 ± 0.3°.

Comparison of the Two Structures. It should be kept in mind that many features of structure **1** are less accurately determined than those of **2**. Nonetheless, most of the bond lengths and bond angles agree quite well, that is, closely enough that they may be considered not to differ significantly in a chemical sense. The Os–Os distances differ by 0.013 Å, which is roughly 4σ, and hence statistically real by the usual 3σ criterion. However, it is unlikely that this difference is really significant. There is probably somewhat more uncertainty in the value obtained for **1** by least-squares refinement than is suggested by the 3σ criterion since a disordered structure may have some unrecognized systematic bias resulting from an inadequacy in the disorder model.

The only difference between the two results that is well beyond doubt is that between the two twist angles, 17.5° in **1** and 5.5° in **2**. Again, because of the possibility that the disorder model is not fully correct, there may be unrecognized error in the former.

It is probably best to place confidence mainly in the structure of **2** when choosing molecular parameters to quote, or to use in electronic structure calculations. Since the Os≡Os triple bond itself offers no barrier to internal rotation, it is not unreasonable that some variability in the twist angle should occur as intermolecular packing forces change from compound to compound. Nevertheless a change from 5.5 to 17.5° is, perhaps, larger than one might have expected.

The question of why there is a twist at all is not easy to answer unambiguously, but it is also not a critical one. Even in cases where there are quadruple bonds, the δ components of which impose a barrier that favors an eclipsed conformation, there are often significant twist angles when the molecules are not subject to any crystallographic symmetry constraint favoring an eclipsed conformation. Examples are Mo_2(1,3-diphenyltriazine)$_4$[13] (10.5°) and $Re_2Cl_4(O_2CCH_3)_2$[14] (5.8°).[14] In the present case one might expect that an intramolecular force causing a twist might be the

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Table VI. Bond Angles (Deg) in $Os_2(hp)_4Cl_2 \cdot 2CH_3CN$ (2)

Os(1)-Os(2)-Cl(2)	177.4 (1)	N(4)-Os(1)-Cl(1)	92.1 (4)
N(1)	87.0 (4)	O(1)	88.2 (5)
N(3)	87.3 (4)	O(3)	91.2 (5)
O(2)	91.5 (4)	N(4)-C(41)-O(4)	119 (2)
O(4)	89.9 (3)	C(42)	123 (2)
Os(2)-Os(1)-Cl(1)	178.5 (1)	N(4)-C(45)-C(44)	121 (2)
N(2)	87.5 (4)	O(1)-Os(1)-Cl(1)	88.1 (4)
N(4)	88.5 (4)	O(3)	178.2 (5)
O(1)	90.5 (3)	O(1)-C(11)-C(12)	121 (2)
O(3)	91.1 (3)	O(2)-Os(2)-Cl(2)	91.1 (4)
N(1)-Os(2)-Cl(2)	92.9 (4)	O(4)	178.2 (5)
N(3)	174.3 (6)	O(2)-C(21)-C(22)	124 (2)
O(2)	90.4 (6)	O(3)-Os(1)-Cl(1)	90.3 (4)
O(4)	88.5 (5)	O(3)-C(31)-C(32)	120 (2)
N(1)-C(11)-O(1)	118 (2)	O(4)-Os(2)-Cl(2)	87.5 (3)
C(12)	121 (2)	O(4)-C(41)-C(42)	118 (2)
N(1)-C(15)-C(14)	120 (2)	C(11)-N(1)-C(15)	119 (2)
N(2)-Os(1)-Cl(1)	91.9 (5)	C(11)-C(12)-C(13)	121 (2)
N(4)	175.9 (6)	C(12)-C(13)-C(14)	119 (2)
O(1)	91.2 (5)	C(13)-C(14)-C(15)	120 (2)
O(3)	89.7 (5)	C(21)-N(2)-C(25)	120 (2)
N(2)-C(21)-O(2)	116 (1)	C(22)-C(23)	119 (2)
C(22)	120 (2)	C(22)-C(23)-C(24)	122 (2)
N(2)-C(25)-C(24)	119 (2)	C(23)-C(24)-C(25)	121 (2)
N(3)-Os(2)-Cl(2)	92.7 (4)	C(31)-N(3)-C(35)	119 (2)
O(2)	90.0 (5)	C(32)-C(33)	120 (2)
O(4)	91.2 (5)	C(32)-C(33)-C(34)	116 (2)
N(3)-C(31)-O(3)	118 (2)	C(33)-C(34)-C(35)	123 (2)
C(32)	122 (2)	C(41)-N(4)-C(45)	120 (2)
N(3)-C(35)-C(34)	120 (2)	C(42)-C(43)	116 (2)
		C(42)-C(43)-C(44)	120 (2)
		C(43)-C(44)-C(45)	120 (2)
		N(111)-C(111)-C(112)	175 (6)
		N(211)-C(211)-C(212)	171 (5)

Table VII. Table of Selected Torsional Angles for $Os_2(hp)_4Cl_2 \cdot 2CH_3CN$ (2)

atom 1	atom 2	atom 3	atom 4	angle, deg
O(1)	Os(1)	Os(2)	N(1)	−5.1
O(2)	Os(2)	Os(1)	N(2)	−5.9
O(3)	Os(1)	Os(2)	N(3)	−5.8
O(4)	Os(2)	Os(1)	N(4)	−5.2

repulsive interactions between the hydrogen atoms at the 6-positions of the rings and the axial chlorine atoms, which are lessened by the twist. It is pertinent in this connection to point out that for compounds in which axial ligands are expected it is necessary to use the hp rather than the mhp (6-methyl-2-hydroxypyridine) ligand since the presence of 6-methyl groups would seriously destabilize even a twisted structure.

Another point worthy of comment is the occurrence of the D_{2d} arrangement of the ligands here, whereas in the stoichiometrically homologous molecule[7] $Re_2(hp)_4Cl_2$, the arrangement has C_{2h} symmetry with like donors being cis on each metal ion. We cannot suggest any simple explanation for this difference, but it should be noted that both arrangements have often been found in the past. Thus, in the $M_2(mhp)_4$ compounds[15,16] as well as in those containing hydroxypyrimidine ligands[17] the D_{2d} arrangement occurs, whereas in the $Cr_2(DMP)_4$ and $Mo_2(DMP)_4$ molecules,[18] where DMP is the 2,6-dimethoxyphenyl anion, the C_{2h} arrangement is found. Indeed, in some recent work on $Rh_2(mhp)_4$ compounds[19] isomers in which *three* ligands are oriented in the same direction have been found.

The assignment of a bond order of 3 to the Os–Os bond is straightforward within the conceptual framework that has been built up for compounds of this type.[1,2] The $Os_2(hp)_4Cl_2$ molecule is a straightforward example of the $\sigma^2\pi^4\delta^2\delta^{*2}$ type of triple bond, which was first observed in the $Re_2Cl_4(PR_4)_4$ type molecules. It is to be noted, however, that the Os≡Os bond distance, ~2.35 Å, is somewhat longer than the W≡W bond lengths[2] which are generally in the range 2.26–2.31 Å and appreciably longer than the Re≡Re bonds[2] which are about 2.24 Å. The greater length might be thought due to the presence of the axial chlorine ligands, but this argument is jeopardized by the fact that the quadruple bond in $Re_2(hp)_4Cl_2$ is, if anything, shorter than most other Re—Re quadruple bonds.

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Supplementary Material Available: Tables of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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