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# Synthesis, Spectroscopy, and X-ray Structure of $Os_2Cl(chp)_4$: An Unusual $Os_2^{5+}$ Complex with a Polar Arrangement of 6-Chloro-2-hydroxypyridinato Ligands and One Axial Chloride

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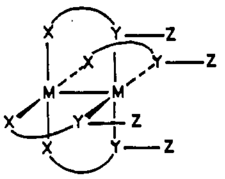
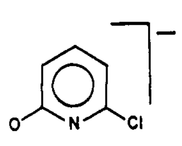
The compound $Os_2Cl(chp)_4$ has been prepared from the melt reaction of $Os_2Cl_2(O_2CCH_3)_4$ with 6-chloro-2-hydroxypyridine (Hchp) at 145 °C. The neutral $Os_2^{5+}$ complex contains a polar arrangement of chp ligands and a single axial chloride. This molecule represents the first structurally characterized compound with an Os–Os bond order of 2.5. Another product of the reaction is $Os_2Cl_4(chp)_2L$ where L is either pyridine or water, depending upon the conditions used to crystallize the compound. Details of the characterization of these species are reported in the paper following this one. Dark brown, air-stable crystals of composition $Os_2Cl(chp)_4 \cdot 2(CH_3)_2CO$ were grown from a solution of acetone–diethyl ether (2:1). The crystallographic data are as follows: triclinic, space group $P\bar{1}$, $a = 9.226$ (1) Å, $b = 13.168$ (2) Å, $c = 14.396$ (2) Å, $\alpha = 95.4$ (1)°, $\beta = 106.7$ (1)°, $\gamma = 100.7$ (1)°, $V = 1624.9$ (4) Å$^3$, $Z = 2$. The structure was refined to $R = 0.038$ ($R_w = 0.059$). The Os–Os distance is 2.348 (1) Å, Os(1)–Cl(axial) = 2.433 (2) Å, Os–O(av) = 2.002 [6] Å, Os–N(av) = 2.088 [6] Å. The molecule is twisted from an ideal eclipsed conformation by approximately 15°. The two acetone molecules are present as solvent of crystallization and do not interact with the diosmium unit. The title compound was also investigated by a variety of methods including infrared, UV–visible, and ESR spectroscopy. The electrochemistry, as determined by cyclic voltammetry, reveals two reversible processes; $E_{1/2}(ox) = +0.90$ V and $E_{1/2}(red) = -0.60$ V vs. Ag/AgCl at room temperature. The low-temperature ESR spectrum (−196 °C) is consistent with that reported for other $Ru^{II}Ru^{III}$ and $Os^{II}Os^{III}$ dinuclear complexes whose magnetic properties are indicative of a triplet contribution to the ground state. A room-temperature measurement (Evans' method) gave a magnetic moment of 2.90 $\mu_B$, also consistent with earlier results.

## Introduction

During the last year, this group has reported a number of interesting diruthenium[1-4] and diosmium[5-8] complexes containing various bidentate oxygen and nitrogen donor ligands. Several of these multiply bonded diruthenium compounds were found to contain an entirely polar (also called 4:0) arrangement of ligands,[3] illustrated schematically as I. This leads to a blocked axial site and prevents the formation of a polymeric structure.[4] The complex $Ru_2Cl(hp)_4(Hhp)$ (hp = 2-hydroxypyridinate)[3] contains the 4:0 arrangement of hp ligands and possesses an axial Hhp ligand that is hydrogen-bonded to one of the bridging hp groups. In another example, $Ru_2Cl(PhNpy)_4$ (PhNpy = 2-anilinopyridine),[3] one Ru center is bonded to four pyridine atoms and to one axial chloride, whereas the axial site of the second Ru atom is blocked by the pendant phenyl groups.



I



(chp)
II

The most notable of these polar complexes, however, is the recently reported compound $Ru_2Cl(chp)_4$ (chp = 6-chloro-2-hydroxypyridinate, II), in which the four oxygen atoms are bonded to the same Ru center in a "head-to-head" fashion, an unprecedented bonding situation for four chloro-substituted hydroxypyridine ligands. Complexes of the formula $M_2(chp)_4$ have been reported for Cr, Mo, and W, and the arrangement of the four bridging ligands is such that each metal is coordinated to two oxygen atoms and two nitrogen atoms in the usual 2:2 arrangement.[9,10] The crystal structure of the polar $Ru_2Cl(chp)_4$ complex revealed close contact of the four chlorines on the $Ru^{II}$ center, and the ligands possess a considerable torsional twist to alleviate the steric interaction.

In contrast to the diruthenium complexes, which preferably exist as $Ru^{II}Ru^{III}$ species, diosmium chemistry is, with a few recently reported exceptions, limited to the $Os_2^{6+}$ dinuclear oxidation state. There exists one report of diosmium(II,III) complexes, by Walton et al.,[11] who prepared salts of the type $[(\eta^5\text{-}C_5H_5)_2Co][Os_2Cl_2(hp)_4]$ and $[(\eta^5\text{-}C_5H_5)_2Co][Os_2Cl_2(O_2CR)_4]$ (R = $C_2H_5$, $C_3H_7$) from the cobaltocene reduction of the parent $Os^{III}Os^{III}$ compounds. These salts were characterized by their spectroscopic, magnetic, and electrochemical properties, and they are expected to be structurally analogous to their neutral precursors.

In this paper we now report the synthesis, electrochemistry, spectroscopic properties, and X-ray crystal structure of the first neutral $Os^{II}Os^{III}$ complex. In $Os_2Cl(chp)_4$, one of the original axial chlorides is absent, the vacant site has been blocked by the four chlorine atoms of the chp ligands, and an overall reduction has taken place. This is the second example of a multiply bonded diosmium complex possessing only one axial ligand, the other example being the unusual asymmetric anilinopyridine compound $Os_2Cl_3(PhNpy)_3$.[5] The present case represents the first structurally characterized diosmium compound with an $Os_2^{5+}$ core and a formal bond order of 2.5.

## Experimental Section

**Starting Materials.** $Os_2Cl_2(O_2CCH_3)_4$ was prepared in ca. 60% yield by the method reported in the literature.[12] Osmium tetraoxide was purchased from Alfa Products, and the ligand 6-chloro-2-hydroxypyridine

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(Hchp) was obtained from Aldrich Chemical Co. All solvents were dried and freshly distilled prior to use.

**Preparation of $Os_2Cl(chp)_4$.** $Os_2Cl_2(O_2CCH_3)_4$ (0.100 g, 0.145 mmol) was ground to a fine powder along with 0.80 g (6.2 mmol) of Hchp, and the solids were sealed in a Pyrex tube. The reaction tube was heated to 145 °C in an oil bath for 6 h. During this period, the materials melted to form a black solution that solidified to a dark brown residue upon cooling to room temperature. The crude product was extracted with dichloromethane to yield a yellow-brown filtrate and an insoluble dark solid. The solution was evaporated to dryness, and the resulting brown material was washed with copius amounts of diethyl ether to remove excess Hchp; yield 60 mg (42%). Anal. Calcd for $Os_2Cl_5N_4O_4C_{20}H_{12}$: C, 25.83; H, 1.30. Found: C, 25.99; H, 1.45. IR data (Nujol mull, KBr): 1595 s, 1525 m, 1335 m, 1165 m, 1018 w, 935 w, 790 s, 730 s, 695 s, 635 w $cm^{-1}$ (s = strong, m = medium, w = weak).

The $Os_2Cl(chp)_4$ complex was recrystallized from dichloromethane–hexane, and large, single crystals were grown by a slow diffusion of diethyl ether into an acetone solution of the compound. The complex appears to be indefinitely stable both in the solid state and in the solution.

**Preparation of $Os_2Cl_4(chp)_2(H_2O)\cdot(CH_3)_2CO$.** The method of synthesis is very similar to the one described for the preparation of $Os_2Cl(chp)_4$. Experiments carried out in sealed Pyrex tubes lead to higher yields of $Os_2Cl_4(chp)_2(L)$, at the expense of the polar complex, $Os_2Cl(chp)_4$, whereas reactions performed in a Schlenk tube under a dinitrogen atmosphere produce more of the $Os_2Cl(chp)_4$ product. In a typical experiment, 200 mg (0.29 mmol) of $Os_2(O_2CCH_3)_4Cl_2$ was ground to a fine powder together with 1.2 g (9.3 mmol) of 6-chloro-2-hydroxypyridine. The solids were then sealed in a Pyrex tube and heated to 145 °C in an oil bath for 12 h. The reaction mixture was cooled, and the contents of the tube were stirred vigorously with 100 mL of diethyl ether for 1 h. The diethyl ether was decanted, and the procedure was repeated. The reaction mixture was filtered, and the solids were vacuum-dried. This procedure effectively removes any unreacted Hchp ligand. The polar complex, $Os_2(chp)_4Cl$, was extracted with two 20-mL portions of dichloromethane. The remaining residue was stirred with 50 mL of reagent-grade acetone along with 0.5 mL of water, and the solution was filtered through a medium-porosity frit. There is usually a small amount (10–20 mg) of $Os_2(O_2CCH_3)_4Cl_2$ left on the frit. The dark purple filtrate was left to evaporate to a low volume, during which time it produced a crop of purple crystals. The solution was filtered, and the crystals were washed with cold acetone and diethyl ether and finally vacuum-dried. The yield is typically 100 mg or 45% (based upon reacted $Os_2(O_2CCH_3)_4Cl_2$). The complex is indefinitely stable in the solid state, but solutions exposed to air decompose over a period of a few days. Anal. Calcd for $Os_2Cl_6O_4N_2C_{13}H_3$: C, 18.25; H, 1.65. Found: C, 18.60; H, 1.73. Electronic spectrum (800–300 nm, acetone solvent): $\lambda_{max}$ = 549 nm ($\epsilon$ = 3440 $M^{-1}$ $cm^{-1}$), $\lambda_{max}$ = 390 nm (sh), $\lambda_{max}$ = 330 nm ($\epsilon$ = 10 200 $M^{-1}$ $cm^{-1}$). IR spectrum, KBr disk (4000–400 $cm^{-1}$): 3440 br, 3100 w, 1665 m, 1600 s, 1535 m, 1435 s, 1388 w, 1340 m, 1180 m, 1028 w, 950 m, 930 w, 808 w, 792 m, 730 m, 640 m $cm^{-1}$ (br = broad, s = stong, m = medium, w = weak).

**Preparation of $Os_2Cl_4(chp)_2(py)$.** $Os_2Cl_4(chp)_2(H_2O)\cdot(CH_3)_2CO$, 50 mg (0.058 mmol) was dissolved in 25 mL of dry acetone in a Schlenk tube. To this was added 0.5 mL of freshly distilled, dry pyridine, and the solution was left undisturbed for 3 days. After this time, the reaction mixture was a pale red, and the product had crystallized on the walls of the Schlenk tube. It was collected by filtration, washed with acetone followed by hexane, and vacuum-dried. The yield is ca. 80–90%. $Os_2Cl_4(chp)_2(py)$ is air-stable and insoluble in most common solvents with the exception of $CH_2Cl_2$, in which it is only sparingly soluble. Anal. Calcd for $Os_2Cl_6O_2N_3C_{15}H_{11}$: C, 20.98, H, 1.29. Found: C, 21.03; H, 1.36. Electronic spectrum (800–300 nm, $CH_2Cl_2$ solvent): $\lambda_{max}$ = 555 nm ($\epsilon$ = 2820 $M^{-1}$ $cm^{-1}$), $\lambda_{max}$ = 330 nm ($\epsilon$ = 9090 $M^{-1}$ $cm^{-1}$), $\lambda_{max}$ = 302 nm ($\epsilon$ = 9180 $M^{-1}$ $cm^{-1}$). IR spectrum, KBr disks (4000–400 $cm^{-1}$): 3100 w, 1600 s, 1530 m, 1450 w, 1432 s, 1385 m, 1340 m, 1225 m, 1180 m, 1070 m, 1025 m, 950 m, 930 m, 810 m, 765 w, 730 m, 695 w, 640 m $cm^{-1}$ (s = strong, m = medium, w = weak).

Details of the spectroscopic properties and molecular structures of the compounds $Os_2Cl_4(chp)_2L$ (L = py, $H_2O$) can be found in the paper following this one.

**Measurements.** Elemental analyses were performed by Galbraith Laboratories, Inc. Infrared spectra were recorded as Nujol mulls between KBr plates or as KBr disks on a Perkin-Elmer 785 spectrophotometer. The electronic spectra were measured on dichloromethane solutions (HPLC grade) with a Cary 17D spectrophotometer. Electrochemical measurements were done with a Bioanalytical Systems Inc., model BAS100 Electrochemical Analyzer in conjunction with a Baush and Lomb, Houston Instruments Model DMP40 digital plotter. Experiments were carried out in dichloromethane containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as a supporting electrolyte. A three-electrode cell configuration was used, with a platinum disk, Model BAS MF 2032, and a platinum wire as a working and auxiliary electrode, respectively. A BAS MF 2020 Ag/AgCl cell was used 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 and are uncorrected for the junction potentials. Magnetic measurements were made in solution at room temperature by the Evans method[13] on a Varian EM 390 spectrometer. X-Band ESR spectra were obtained on frozen dichloromethane solutions at −196 °C with a Varian E-6S spectrometer.

**Table I.** Crystal Data, Data Collection Parameters, and Least-Squares Residuals for $Os_2Cl(chp)_4\cdot 2(CH_3)_2CO$

| | |
|---|---|
| formula | $Os_2Cl(C_5H_3NOCl)_4\cdot 2(CH_3)_2CO$ |
| fw | 1046.165 |
| space group | $P\bar{1}$ |
| systematic absences | none |
| $a$, Å | 9.226 (1) |
| $b$, Å | 13.168 (2) |
| $c$, Å | 14.396 (2) |
| $\alpha$, deg | 95.4 (1) |
| $\beta$, deg | 106.7 (1) |
| $\gamma$, deg | 100.7 (1) |
| $V$, Å$^3$ | 1624.9 (4) |
| $Z$ | 2 |
| $d_{calcd}$, g/cm$^3$ | 2.073 |
| cryst size, mm | 0.50 × 0.60 × 0.12 |
| $\mu$(Mo K$\alpha$), $cm^{-1}$ | 15.76 |
| data collcn instrument | Syntex P3 |
| Radiation (monochromated in incident beam) | Mo K$\alpha$ ($\gamma$ = 0.710 73 Å) |
| orientation reflcns: no.; range ($2\theta$), deg | 25; $24 < 2\theta < 36$ |
| temp, °C | 25 ± 1 |
| scan method | $\omega$–$2\theta$ |
| data collcn range ($2\theta$), deg | 4–50 |
| no. of unique data; total with $F_o^2 > 3\sigma(F_o^2)$ | 4946; 4602 |
| no. of params refined | 348 |
| trans factors: max; min | 99.79; 27.96 |
| $R^a$ | 0.038 |
| $R_w{}^b$ | 0.059 |
| quality-of-fit indicator$^c$ | 1.399 |
| largest shift/esd, final cycle | 0.10 |
| largest peak, e/Å$^3$ | 1.96 |

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

**X-ray Crystallographic Procedures.** The structure of a single crystal of $Os_2Cl(chp)_4\cdot 2(CH_3)_2CO$ was determined by application of general procedures that have been fully described elsewhere.[14,15] The pertinent crystallographic data are summarized in Table I. Positional parameters and important bond distances and angles for the structure may be found in Tables II and III, respectively.

A very dark, thin crystal of $Os_2Cl(chp)_4$ of approximate dimensions 1.20 × 0.60 × 0.12 mm was cleaved along a visible twinning boundary to yield two triangular fragments. One of them of size 0.60 × 0.50 × 0.12 mm was mounted on the tip of a glass fiber. All diffraction data were collected on a Syntex P3 autodiffractometer equipped with graphite-monochromated Mo K$\alpha$ ($\lambda$ = 0.710 73 Å) radiation. The unit cell was indexed on 25 strong reflections in the range $24 < 2\theta < 36°$ that were selected from the data collection list. The positions of two Os atoms were obtained from a Patterson map, and the remaining non-hydrogen atoms were located from alternating least-squares refinements and difference Fourier maps. During the refinement, it became apparent that absorption effects still affected the results despite an earlier absorption correction based on $\psi$ scans. Therefore, the program DIFABS was applied to the data.[16] This correction eliminated most of the heavy-atom ghosts and

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**Table II.** Positional Parameters and Their Estimated Standard Deviations for $Os_2Cl(chp)_4 \cdot 2(CH_3)_2CO^a$

| atom | *x* | *y* | *z* | *B*, Å$^2$ |
|---|---|---|---|---|
| Os(1) | –0.06091 (4) | 0.26100 (3) | 0.14710 (2) | 2.195 (7) |
| Os(2) | 0.17930 (4) | 0.33522 (2) | 0.26692 (2) | 2.011 (7) |
| Cl(1) | 0.2941 (3) | 0.4890 (2) | 0.4864 (2) | 4.03 (6) |
| Cl(2) | 0.5489 (3) | 0.3360 (2) | 0.2893 (2) | 4.04 (6) |
| Cl(3) | 0.4418 (3) | 0.5621 (2) | 0.3140 (2) | 4.11 (6) |
| Cl(4) | 0.4004 (3) | 0.2584 (2) | 0.4633 (2) | 4.22 (6) |
| Cl(5) | –0.3091 (3) | 0.1861 (2) | 0.0215 (2) | 3.76 (6) |
| O(1) | –0.1371 (7) | 0.3882 (5) | 0.1767 (4) | 2.9 (1) |
| O(2) | 0.0153 (7) | 0.1337 (5) | 0.1183 (5) | 2.9 (1) |
| O(3) | 0.0196 (7) | 0.3266 (5) | 0.0458 (4) | 2.8 (1) |
| O(4) | –0.1388 (7) | 0.1992 (5) | 0.2517 (4) | 3.0 (1) |
| O(5) | 0.713 (1) | 0.783 (1) | 0.2371 (9) | 8.7 (3)* |
| O(6) | 0.220 (5) | 0.796 (4) | 0.254 (3) | 18 (1)* |
| N(1) | 0.0725 (8) | 0.4460 (5) | 0.3183 (5) | 2.3 (1) |
| N(2) | 0.2685 (8) | 0.2221 (5) | 0.2035 (5) | 2.2 (1) |
| N(3) | 0.2283 (8) | 0.4336 (5) | 0.1697 (5) | 2.3 (1) |
| N(4) | 0.1106 (8) | 0.2350 (5) | 0.3578 (5) | 2.3 (1) |
| C(1) | –0.064 (1) | 0.4564 (6) | 0.2558 (7) | 2.8 (2) |
| C(2) | –0.136 (1) | 0.5398 (7) | 0.2764 (7) | 3.4 (2) |
| C(3) | –0.068 (1) | 0.6089 (9) | 0.3634 (9) | 4.7 (3) |
| C(4) | 0.075 (1) | 0.5953 (8) | 0.4296 (8) | 4.3 (3) |
| C(5) | 0.132 (1) | 0.5141 (7) | 0.4047 (7) | 2.9 (2) |
| C(6) | 0.166 (1) | 0.1368 (7) | 0.1419 (7) | 3.0 (2) |
| C(7) | 0.215 (1) | 0.0514 (7) | 0.1043 (7) | 3.3 (2) |
| C(8) | 0.369 (1) | 0.0563 (8) | 0.1241 (8) | 3.9 (2) |
| C(9) | 0.479 (1) | 0.1454 (8) | 0.1863 (7) | 3.5 (2) |
| C(10) | 0.421 (1) | 0.2232 (7) | 0.2202 (6) | 2.5 (2) |
| C(11) | 0.139 (1) | 0.4060 (7) | 0.0710 (6) | 2.6 (2) |
| C(12) | 0.173 (1) | 0.4616 (8) | –0.0016 (7) | 3.2 (2) |
| C(13) | 0.293 (1) | 0.5463 (8) | 0.0257 (8) | 4.1 (3) |
| C(14) | 0.384 (1) | 0.5787 (8) | 0.1271 (7) | 3.9 (2) |
| C(15) | 0.341 (1) | 0.5207 (7) | 0.1890 (7) | 3.2 (2) |
| C(16) | –0.043 (1) | 0.1942 (7) | 0.3356 (7) | 2.8 (2) |
| C(17) | –0.107 (1) | 0.1431 (8) | 0.4028 (8) | 3.9 (2) |
| C(18) | –0.006 (1) | 0.1309 (8) | 0.4915 (7) | 4.3 (3) |
| C(19) | 0.155 (1) | 0.1656 (7) | 0.5114 (7) | 3.7 (2) |
| C(20) | 0.205 (1) | 0.2154 (7) | 0.4433 (7) | 3.3 (2) |
| C(21) | 0.752 (2) | 0.941 (2) | 0.178 (1) | 9.5 (5)* |
| C(22) | 0.729 (2) | 0.828 (1) | 0.172 (1) | 5.9 (3)* |
| C(23) | 0.717 (2) | 0.767 (2) | 0.074 (1) | 9.1 (5)* |
| C(24) | 0.192 (4) | 0.930 (3) | 0.339 (3) | 9 (1)* |
| C(25) | 0.252 (4) | 0.877 (3) | 0.319 (3) | 8.6 (9)* |
| C(26) | 0.395 (5) | 0.930 (3) | 0.349 (3) | 11 (1)* |

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

reduced the number of peaks above 1 e/Å$^3$ in the difference Fourier map from 20 to 8. The entire structure, with the exception of the acetone solvent molecules, was refined anisotropically. One of the acetone molecules was badly disordered, and simple models were unsuccessful in defining the nature of the disorder. Consequently, the atoms in this acetone were refined at half occupancy. There is, however, electron density remaining in this area, as determined by inspection of the last difference Fourier. In a final cycle, 4602 data over $3\sigma$ were used to refine 348 parameters to give $R = 0.038$ and $R_w = 0.059$.

## Results and Discussion

**Preparation.** The action of molten Hchp upon $Os_2Cl_2(O_2CCH_3)_4$ leads to the displacement of the four acetate ligands along with the loss of an axial chloride to give the title compound in 40% yield. This type of melt reaction has been successfully employed to prepare, in essentially quantitative yield, diruthenium compounds of chp and other related ligands containing three-atom bridges.[3,17] In the present example, the reaction is obviously more complex since an overall dimetal reduction has taken place to yield $Os_2Cl(chp)_4$, a derivative of an $Os_2^{5+}$ dinuclear core. Furthermore, there is another major product, an $Os_2^{6+}$ species, which is the subject of the paper following this one.

**Table III.** Selected Bond Distances (Å) and Angles (deg) for $Os_2Cl(chp)_4 \cdot 2(CH_3)_2CO^a$

| atom 1 | atom 2 | dist | atom 1 | atom 2 | dist |
|---|---|---|---|---|---|
| Os(1) | Os(2) | 2.348 (1) | Cl(2) | C(10) | 1.726 (7) |
| Os(1) | Cl(5) | 2.433 (2) | Cl(3) | C(15) | 1.749 (8) |
| Os(1) | O(1) | 1.989 (5) | Cl(4) | C(20) | 1.718 (9) |
| Os(1) | O(2) | 1.988 (5) | O(1) | C(1) | 1.302 (9) |
| Os(1) | O(3) | 2.012 (6) | O(2) | C(6) | 1.320 (10) |
| Os(1) | O(4) | 2.021 (6) | O(3) | C(11) | 1.306 (9) |
| Os(2) | N(1) | 2.098 (6) | O(4) | C(16) | 1.290 (10) |
| Os(2) | N(2) | 2.088 (6) | N(1) | C(1) | 1.362 (11) |
| Os(2) | N(3) | 2.081 (6) | N(2) | C(6) | 1.371 (10) |
| Os(2) | N(4) | 2.086 (6) | N(3) | C(11) | 1.396 (10) |
| Cl(1) | C(5) | 1.725 (9) | N(4) | C(16) | 1.349 (10) |

| atom 1 | atom 2 | atom 3 | angle |
|---|---|---|---|
| Os(2) | Os(1) | Cl(5) | 179.14 (6) |
| Os(2) | Os(1) | O(1) | 89.8 (2) |
| Os(2) | Os(1) | O(2) | 90.0 (2) |
| Os(2) | Os(1) | O(3) | 89.5 (2) |
| Os(2) | Os(1) | O(4) | 89.2 (2) |
| O(1) | Os(1) | O(3) | 90.0 (2) |
| O(1) | Os(1) | O(4) | 88.8 (2) |
| O(2) | Os(1) | O(3) | 90.2 (2) |
| O(2) | Os(1) | O(4) | 90.9 (2) |
| Os(1) | Os(2) | N(1) | 87.7 (2) |
| Os(1) | Os(2) | N(2) | 87.2 (2) |
| Os(1) | Os(2) | N(3) | 87.9 (2) |
| Os(1) | Os(2) | N(4) | 87.6 (2) |
| N(1) | Os(2) | N(3) | 88.2 (2) |
| N(1) | Os(2) | N(4) | 89.8 (2) |
| N(2) | Os(2) | N(3) | 89.8 (2) |
| N(2) | Os(2) | N(4) | 91.7 (2) |
| O(1) | C(1) | N(1) | 120.7 (7) |
| Cl(1) | C(5) | N(1) | 114.8 (6) |
| O(2) | C(6) | N(2) | 119.1 (7) |
| Cl(2) | C(10) | N(2) | 115.6 (5) |
| O(3) | C(11) | N(3) | 118.8 (7) |
| O(4) | C(16) | N(4) | 121.1 (7) |
| Cl(4) | C(20) | N(4) | 115.2 (7) |

$^a$Numbers in parentheses are estimated standard deviations in the least significant digits.

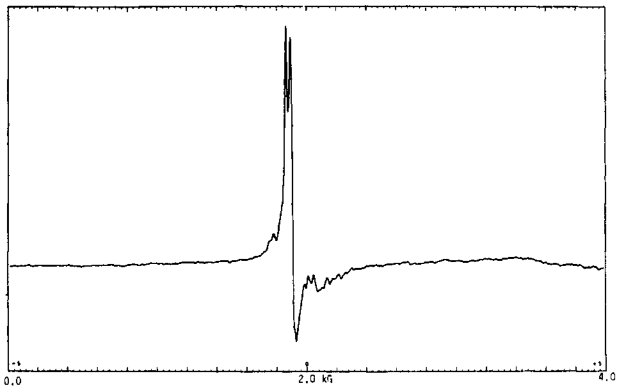

Figure 1. X-Band ESR spectrum of $Os_2Cl(chp)_4$ in dichloromethane at −196 °C.

**Spectroscopic and Magnetic Properties.** The $Os_2Cl(chp)_4$ compound, formally of the $Os_2^{5+}$ dinuclear oxidation state, is inherently paramagnetic ($d^5$–$d^6$), and not surprisingly it does not exhibit a $^1H$ NMR signal. The complex also does not give a room-temperature ESR signal; however, at −196 °C it displays a very well-defined spectrum (see Figure 1). The signal is centered at ~1760 G and closely resembles the spectrum reported by Walton et al. for $[(\eta^5\text{-}C_5H_5)_2Co][Os_2Cl_2(hp)_4]$.[11] These authors concluded, by a reasonable analogy to the $Ru_2(O_2CC_3H_7)_4Cl$ system,[18] that the spectral features resulted from a large zero-field splitting between the $|\pm^3/_2\rangle$ and $|\pm^1/_2\rangle$ states. Our present results are in accord with these earlier studies, and they demonstrate,

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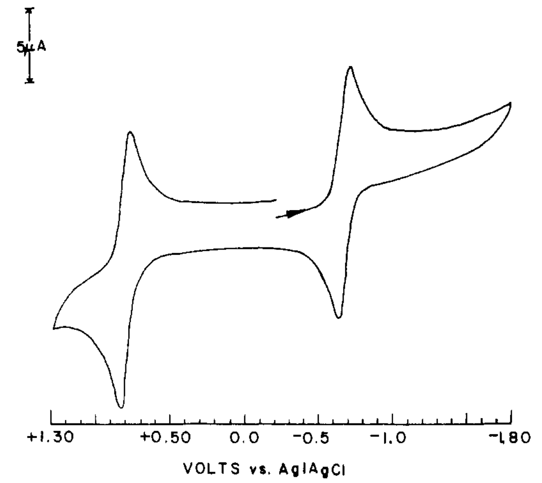

**Figure 2.** Cyclic voltammogram of $Os_2Cl(chp)_4$ (measured at 200 mV/s in 0.2 M TBAH–$CH_2Cl_2$ at a Pt-disk electrode).

again, that an $S = {}^3/_2$ contribution to the ground state exists even at the low temperature of −196 °C.

A magnetic moment determination by the Evans method for $Os_2Cl(chp)_4$ at 298 K gave $\mu_{eff} = 2.90\ \mu_B$. This value is intermediate between those expected for $S = {}^3/_2$ and $S = {}^1/_2$, suggesting that, at room temperature, electronic states derived from both the $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*2}$ and $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*1}$ (or $\sigma^2\pi^4\delta^2\pi^{*3}$) configurations are present. The temperature dependence of the magnetic moment of $Os_2^{5+}$ complexes was noted in the previous study,[11] but the temperature ranges that are accessible by using the solution Evans method are not large enough to define clearly the nature of this dependence. We plan to carry out a study of the solid-state magnetic susceptibilities of $Os_2Cl(chp)_4$ and of several other known diosmium complexes. These results, determined over a wide temperature range, should provide a basis for a comprehensive treatment of the electronic properties of these compounds.

The electronic absorption spectrum of $Os_2Cl(chp)_4$ was recorded in dichloromethane, and it exhibits bands at 412 nm ($\epsilon$ = 3800 $M^{-1}$ $cm^{-1}$) and 292 nm ($\epsilon$ = 21 400 $M^{-1}$ $cm^{-1}$) as well as a shoulder at 319 nm. The spectrum of the analogous $Ru_2Cl(chp)_4$ compound is markedly different, with bands occuring at 530 nm ($\epsilon$ = 4740), 440, 480, 340 (sh), and 680 (br) nm.[4]

**Electrochemistry.** A cyclic voltammetric measurement on a 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH)–dichloromethane solution of $Os_2Cl(chp)_4$ revealed two reversible couples in the range from +2.0 to −2.0 V vs. Ag/AgCl (see Figure 2). The complex exhibits a reversible one-electron oxidation at $E_{1/2}$ = +0.90 V vs. Ag/AgCl and a reversible one-electron reduction at $E_{1/2}$ = −0.60 V vs. Ag/AgCl. The couples correspond to $Os^{II}Os^{III} - e^- \rightarrow Os^{III}Os^{III}$ and $Os^{II}Os^{III} + e^- \rightarrow Os^{II}Os^{II}$ processes, respectively. In contrast, the redox chemistry of the triply bonded $Os_2^{6+}$ compounds such as $Os_2Cl_2(O_2CR)_4$ and $Os_2Cl_2(hp)_4$ consists of a very accessible, reversible one-electron reduction located at ca. +0.30 V vs. SCE.[11] This reduction can be achieved chemically with cobaltocene as the reducing agent. This allows the preparation of the monoanion complex, formally containing $Os_2^{5+}$, which exhibits an oxidation couple that is located at the same $E_{1/2}$ value as the reduction potential of the neutral complex.

Electrochemical studies of the $Os_2^{6+}$ compounds $Os_2Cl_2(PhCONH)_4$[8] and $Os_2Cl_3(PhNpy)_3$[5] have revealed similar behavior, and it has been noted that an increase in formal reduction potential for the $Os^{III}Os^{III}/Os^{II}Os^{III}$ couple follows the order of decreasing Os≡Os triple-bond lengths in an approximately linear fashion.[8] In the present case, the neutral $Os_2^{5+}$ compound $Os_2Cl(chp)_4$ is appreciably stabilized with respect to oxidation to the $Os_2^{6+}$ species ($E_{1/2}$ = +0.90 V vs. Ag/AgCl). On the other hand, the reduction at $E_{1/2}$ = −0.60 V, which corresponds to the formation of an $Os^{II,II}$ species (formally containing an Os=Os double bond) is considerably more accessible in $Os_2Cl(chp)_4$ than in the known diosmium(III) complexes. These $Os_2^{6+}$ compounds exhibit a relatively inaccessible reduction at −1.0 V or greater.

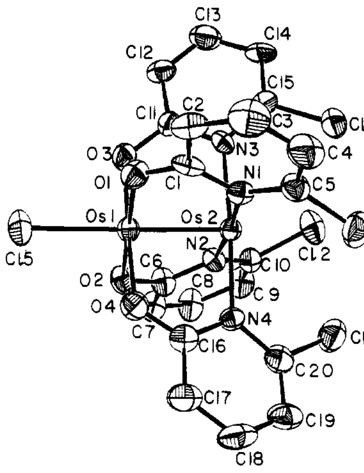

**Figure 3.** ORTEP drawing of the $Os_2Cl(chp)_4$ molecule with the atom-labeling scheme. Atoms are represented by thermal vibration ellipsoids at the 50% level.

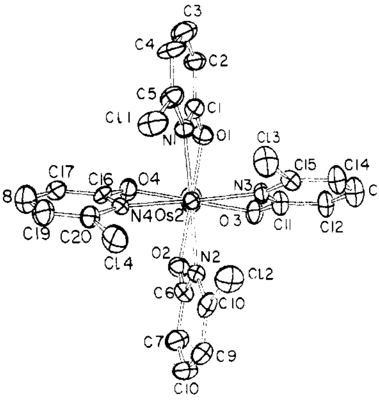

**Figure 4.** View down the Os–Os bond axis, showing the torsional twist of the chp ligands.

**Table IV.** Comparison of Important Distances (Å) and Angles (deg) for the Two Polar $M_2Cl(chp)_4$ Complexes (M = Ru, Os)

| | $Os_2Cl(chp)_4$ | $Ru_2Cl(chp)_4$ |
|---|---|---|
| M–M | 2.348 (1) | 2.281 (1) |
| M–Cl(ax) | 2.433 (2) | 2.443 (2) |
| M–O(av) | 2.002 (6) | 2.002 (5) |
| M–N(av) | 2.088 (6) | 2.085 (6) |
| torsion angle | 15 | 19 |

**Molecular Structure.** The positional parameters for $Os_2Cl(chp)_4{\cdot}2(CH_3)_2CO$ are given in Table II. Selected bond distances and angles are presented in Table III. The labeled ORTEP diagram of the molecule presented in Figure 3 clearly depicts the polar arrangement of chp ligands and shows the single axial chloride bonded to Os(1). The only other reported example of this arrangement of four chp ligands is, as mentioned in the introduction, found in $Ru_2Cl(chp)_4$, which can be compared to and contrasted with the new osmium analogue.[4] Although the diruthenium compound is not crystallographically isomorphous to $Os_2Cl(chp)_4$ ($Ru_2Cl(chp)_4$ is orthorhombic, *Pbcn*), the molecular structures are quite similar with the exception of the M–M distances.

The $Os_2Cl(chp)_4$ molecule does not possess any crystallographically imposed symmetry, and the highest molecular symmetry that can be ascribed to it is $C_4$. As in the $Ru_2Cl(chp)_4$ molecule, the chp ligands are twisted about the Os–Os axis with an average torsional twist angle of 15.2° (see Table IV and Figure 4). This distortion is slightly less than the 18.8° average twist found in the ruthenium compound. This may be due to the slightly larger size of the osmium atoms, which means that the chlorine atoms tend to be further apart. As before, the twisting is assumed to be a means of reducing the repulsive Cl···Cl contacts, although it is not possible to do this to more than a moderate extent without encountering other unfavorable energy factors that limit the twisting. In this case, the final Cl···Cl distances are in the range 3.30–3.35 Å, but they would be shorter if there were no twisting.

The 4:0 or totally polar arrangement makes possible the formation of one strong axial Os–Cl bond in exchange for some Cl···Cl repulsive energy, whereas a 2:2 arrangement would presumably preclude any axial bonding, even though Cl···Cl repulsions would be much less. The axial Os–Cl bond here, with a distance of 2.433 (2) Å, is apparently a fairly strong one and may be compared with those in $Ru_2Cl(chp)_4$ and the $Os_2Cl_2(O_2CR)_4$ compounds.[4,19] The present axial Os–Cl distance is appreciably shorter than those in $Os_2Cl_2(hp)_4$, where they are 2.505 (5) Å.[20] The average Os–O and Os–N distances, 2.002 [6] Å and 2.088 [6] Å, respectively, and the mean angles, Os–Os–O = 89.6 [2]°, O–Os–O(cis) = 89.9 [2]°, and N–Os–N(cis) = 89.8 [2]°, are within the expected ranges.

We may finally turn to a comparison of the present Os–Os bond length, 2.348 (1) Å, with Os–Os distances found in other comparable $Os_2$ compounds. It is 0.034 Å longer than that in the tetraacetate starting material.[19] This is a rather small increase for a bond order decrease of 0.5, but this need not be surprising since the change from $Os_2^{6+}$ to $Os_2^{5+}$ may also increase the overlap in all the bonding orbitals, thus tending to strengthen the bond. Exactly this type of situation where there are countervailing—and nearly offsetting—factors has been thoroughly documented before for the series $[Re_2Cl_4(PMe_2Ph)_4]^{n+}$ ($n$ = 2, 1, 0).[21]

**Acknowledgment.** We thank the National Science Foundation for support.

**Registry No.** $Os_2Cl(chp)_4{\cdot}2(CH_3)_2CO$, 101471-02-7; $Os_2Cl(chp)_4$, 101420-22-8; $Os_2Cl_4(chp)_2(H_2O)$, 101403-87-6; $Os_2Cl_4(chp)_2(py)$, 101403-86-5; $Os_2Cl_2(O_2CCH_3)_4$, 81519-41-7; Os, 7440-04-2.

**Supplementary Material Available:** Full listings of bond angles, bond distances, positional parameters, and anisotropic thermal parameters (6 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (23 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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# Preparation and Structural Characterization of $Os_2Cl_4(chp)_2(L)$ (chp = 6-Chloro-2-hydroxypyridinato; L = $H_2O$, Pyridine): A New Class of $M_2X_4(LL)_2$ Complexes Possessing an Eclipsed Conformation Where LL Is a Substituted Hydroxypyridinato Ligand

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The melt reaction of 6-chloro-2-hydroxypyridine with $Os_2(O_2CCH_3)_4Cl_2$ at 145 °C affords two products. A polar compound, $Os_2(chp)_4Cl$, was recently characterized, and details of the X-ray structure and spectroscopic data are fully described in the preceding paper.[1] We now wish to report the identification of the second product, $Os_2Cl_4(chp)_2$, which has been isolated as two different adducts: $Os_2Cl_4(chp)_2(py)$ (**1**) and $Os_2Cl_4(chp)_2(H_2O){\cdot}(CH_3)_2CO$ (**2**). Crystals of **1** were grown by vapor diffusion of hexane into a solution of the compound in acetone–pyridine (40:1). The crystallographic data for **1** are as follows: monoclinic, space group $C2/c$, $a$ = 14.718 (2) Å, $b$ = 12.860 (3) Å, $c$ = 11.553 (2) Å, $\beta$ = 100.5 (1)°, $V$ = 2150 (1) Å$^3$, $Z$ = 4. The structure was refined to $R$ = 0.027 ($R_w$ = 0.033). The molecule has crystallographically imposed $C_2$ symmetry with a twofold axis lying along the Os–Os bond axis. The Os–Os distance is 2.322 (1) Å, Os(1)–N(axial) = 2.238 (14) Å, Os–Cl(av) = 2.29 (3) Å, Os(1)–N(1) = 2.095 (9) Å, Os(2)–O(1) = 1.980 (8) Å. Crystals of **2** were grown by slow evaporation in air of an acetone solution of the complex. Pertinent crystallographic data are as follows: triclinic, space group $P\bar{1}$, $a$ = 9.445 (2) Å, $b$ = 15.148 (3) Å, $c$ = 7.855 (2) Å, $\alpha$ = 94.92 (2)°, $\beta$ = 98.50 (2)°, $\gamma$ = 75.73 (1)°, $V$ = 1075.7 (4) Å$^3$, $Z$ = 2. The structure was refined to $R$ = 0.039 ($R_w$ = 0.065). The molecule possesses virtual $C_{2v}$ symmetry although there is a lack of crystallographically imposed symmetry. The interstitial acetone molecule interacts significantly with the diosmium unit via hydrogen bonding to the axial water molecule. The hydrogen atoms were not located during the crystallographic refinement, but the distance between the oxygen atoms of acetone and water is only 2.726 Å, clearly indicating the presence of hydrogen bonds. The title compounds are formally derivatives of $[Os_2Cl_8]^{2-}$, a species that has only recently been prepared and structurally characterized.[2a] In addition, **1** and **2** are the first examples of an $Os_2X_4(LL)_2$ class of compounds, a type unknown for platinum metals. Furthermore, there are no reported examples of $M_2X_4(LL)_2$ complexes with an overall eclipsed conformation that contain a substituted hydroxypyridinate anion as the trans bidentate ligand. The electrochemistry of **1** and **2**, as determined by cyclic voltammetry, reveals a reversible reduction process located at $E_{1/2}$ = +0.15 V vs. Ag/AgCl for **1** and $E_{1/2}$ = +0.46 V vs. Ag/AgCl for **2**. A solution of $Os_2Cl_4(chp)_2(py)$ in dichloromethane exhibits a band at 555 nm ($\epsilon$ = 2815 M$^{-1}$ cm$^{-1}$), and an acetone solution of $Os_2Cl_4(chp)_2(H_2O)$ displays an absorption maximum at 549 nm ($\epsilon$ = 3440 M$^{-1}$ cm$^{-1}$).

## Introduction

Early research efforts in the development of multiply bonded dimetal complexes were focused primarily upon transition metals from groups V–VII (5–7)[28] with little attention being directed toward the platinum-group elements.[3] Since the discovery of the first osmium–osmium triple bond, there has been a growing interest in the preparation of new diruthenium[4-7] and diosmium[8-11] systems.

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