Completion of the Series of $M_2(hpp)_4Cl_2$ Compounds from W to Pt: The W, Os, and Pt Compounds

**Rodolphe Clérac,[†] F. Albert Cotton,*[,‡] Lee M. Daniels,[‡] James P. Donahue,[‡]
Carlos A. Murillo,*[,‡,§] and Daren J. Timmons[‡]**

Department of Chemistry, College of Natural Science, Michigan State University,
East Lansing, Michigan 48824, Laboratory for Molecular Structure and Bonding and
Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255, and
Department of Chemistry, University of Costa Rica, Ciudad Universitaria, Costa Rica

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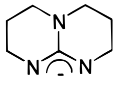
The series of $M_2(hpp)_4Cl_2$ complexes (hpp is the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine) from M = W to M = Pt has been completed by the preparation and characterization of those with M = W, Os, and Pt. $W_2(hpp)_4Cl_2$ (**1**) has a W−W distance of 2.250(2) Å, is diamagnetic, and can be assigned a W−W triple bond based on a $\sigma^2\pi^4$ electron configuration. $Os_2(hpp)_4Cl_2$ (**2**) has an Os−Os distance of 2.379(2) Å and displays a temperature-independent paramagnetism. It can be assigned a $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration. $Pt_2(hpp)_4Cl_2$ has a Pt−Pt distance of 2.440(1) Å and is diamagnetic. A bond order of 1, based on a configuration in which only the σ^* orbital is empty, is consistent with these data.

Introduction

The general utility of the anion of the 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine ligand, **I**, in stabilizing metal−metal multiple bonds has already been established for the following elements: V,[1] Cr,[1] Nb,[2] Mo,[1,3] Ru,[4] Pd,[5] Re,[6] and Ir.[7] The hpp ligand was originally employed because of its superior stability compared to the formamidinate ligands, **II**, but as the chemistry has unfolded it has become clear that it also differs from formamidinate anions electronically to a sufficient extent that it can stabilize M_2^{n+} units not obtainable with formamidinates, e.g., Mo_2^{6+}, Pd_2^{6+}, and Ir_2^{6+}. Thus, our interest in the hpp ligand is now based as much, or more, on its electronic ability to stabilize unusual M_2^{n+} units as on its ability to survive harsh reducing conditions, e.g., Nb_2^{4+}.



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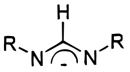

II

It now seems possible that the hpp ligand will be able to give a greater range of M_2^{n+} species than any other ligand, or class of ligands (such as the amidinate anions), has been capable of doing. To explore this possibility, and to increase our understanding of the electronic factors at work, we have undertaken completion of the entire series of $M_2(hpp)_4Cl_2$ compounds, from M = W to M = Pt, which means adding to the already known rhenium and iridium species those of tungsten, osmium, and platinum.

Experimental Section

Metal starting materials were obtained from commercial sources: WCl_4 (Aldrich); $OsCl_3$ (Strem); $PtCl_2$ (Strem). Hhpp was obtained from Fluka and sublimed prior to use. Lihpp was prepared in THF by the deprotonation of Hhpp with MeLi and was used directly without being isolated. $NaEt_3BH$ (1.0 M/toluene) was obtained from Aldrich. Solvents were freshly distilled under N_2 from suitable drying agents. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk line techniques unless otherwise stated. The IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrophotometer as a KBr pellet, UV−vis spectra were recorded on a Cary-17D spectrometer, and the ^1H NMR spectra were collected on a Varian 200 spectrometer. Elemental analyses were done by Canadian Microanalytical Service, Ltd.; the results were satisfactory.

The magnetic susceptibility data were collected on a Quantum Design, model MPMS-5, SQUID (superconducting quantum interference device) housed in the Department of Physics and Astronomy at Michigan State University. Data were collected on a powder sample from 1.8 to 300 K at a field strength of 1000 G. The magnetic susceptibility data were corrected for the sample holder contribution and for the intrinsic diamagnetic contribution (-3×10^{-4} emu/mol), which was estimated from Pascal's constants.[8] At low temperature (between 2 and 10 K), a very small extrinsic paramagnetic impurity was observed corresponding to 0.004% of spin $S = 1/2$.

Preparation of $W_2(hpp)_4Cl_2$, 1. A flask was charged with WCl_4 (0.50 g, 1.54 mmol) and 50 mL of THF. One equivalent of $NaEt_3BH$ was added at room temperature, and the mixture was stirred overnight. The dark green solution was separated from the unreacted WCl_4 by filtration. A solution of Lihpp (2.77 mmol) in 10 mL of THF was added

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[†] Michigan State University.
[‡] Texas A&M University.
[§] University of Costa Rica.

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Table 1. Crystallographic Parameters for $W_2(hpp)_4Cl_2$, **1**, $Os_2(hpp)_4Cl_2$, **2** and $Pt_2(hpp)_4Cl_2$, **3**

	1	**2**·$4CH_2Cl_2$	**3**
empirical formula	$C_{28}H_{48}Cl_2N_{12}W_2$	$C_{32}H_{56}Cl_{10}N_{12}Os_2$	$C_{28}H_{48}Cl_2N_{12}Pt_2$
fw	991.38	1343.79	1013.86
space group	*I*4/*m*	*I*4/*mmm*	*I*4222
a, Å	9.949(2)	13.715(3)	10.4935(6)
c, Å	15.841(2)	12.174(3)	14.615(1)
V, Å^3	1568.2(5)	2289.8(9)	1609.3(2)
Z	2	2	2
d_{calcd}, g cm^{-3}	2.100	1.949	2.092
μ, mm^{-1}	7.543	6.168	8.891
radiation		Mo Kα ($\lambda_\alpha = 0.710\,73$ Å)	
temp, K	213(2)	213(2)	296(2)
residuals: R1,[a] wR2[b]	0.057, 0.114	0.022, 0.060	0.063, 0.118
weight params[b] (*a*, *b*)	0.012, 90.07	0.0, 29.15	0.080, 0.0

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $wR2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$.

via cannula to the W^{III} solution. Some solid was immediately visible; the reaction was stirred for 15 min. Upon standing, the reaction mixture gave brown crystals of **1** (0.03 g) along with some brown powder of **1** (0.21 g). Yield: 45%. One of the brown crystals was used for X-ray diffraction. The solid is only slightly soluble in most organic solvents, thereby making further characterization difficult. The ^{1}H NMR spectrum was obtained after collection of many transients on a dilute sample: (DMSO-d_6, ppm) 3.27 (t, CH_2) 3.18 (t, CH_2), 1.87 (quin, CH_2). IR (KBr, cm^{-1}): 2921 (s), 2850 (s), 1635 (s), 1450 (vs), 1494 (s), 1448 (s), 1387 (s), 1309 (vs), 1217 (s), 1136 (m), 1070 (m), 1033 (m), 880 (w), 752 (s), 734 (m), 418 (w).

Preparation of $Os_2(hpp)_4Cl_2$, 2. In a modification of a published procedure,[9] osmium(III) chloride (0.30 g, 1.0 mmol) and 4 equiv of Hhpp (0.57 g, 4.10 mmol) were refluxed in 20 mL of ethanol overnight. A dark red solid precipitated from the brown solution and was isolated by filtration. The air-stable solid was collected in 34% yield (0.173 g). Crystals were grown by the slow diffusion of hexanes into a dichloromethane solution. ^{1}H NMR ($CDCl_3$, ppm): 10.23 (t, CH_2), 6.11 (quin, CH_2), −2.36 (t, CH_2). IR (KBr, cm^{-1}): 3401 (w), 2961 (m), 1653 (w), 1590 (s), 1532 (m), 1505 (s), 1445 (vs), 1307 (vs), 1262 (s), 1214 (m), 1158 (s), 1098 (vs), 1030 (s), 804 (m), 752 (m), 691 (w), 496 (vw). UV−vis (CH_2Cl_2, nm): 355, 465, 495, 585 (sh).

Preparation of $Pt_2(hpp)_4Cl_2$, 3. A slurry of Lihpp (0.11 g, 0.76 mmol) in 10 mL of toluene was added to a suspension of $PtCl_2$ (0.10 g, 0.38 mmol) in 10 mL of toluene; no reaction was observed when the mixture was stirred overnight. However, when heated to a gentle reflux for 3 h, the solution became substantially red-brown. Although a fair amount of solid remained, the solution was separated from the mixture by filtration through Celite. The addition of 20 mL of hexanes caused the precipitation of a brown-orange solid (0.030 g). A small amount of the solid was dissolved in benzene, and the benzene was allowed to evaporate in air to yield several orange crystals of **3**. A bulk preparation is under development presently and will be reported at a later date.

X-ray Crystallography. The data for **1** and **2** were collected at 213(2) K on a Nonius FAST area-detector system. Typical procedures for our laboratory have been described.[10] Crystals of **1** and **2**·$4CH_2Cl_2$ were refined in space groups *I*4/*m* and *I*4/*mmm*, respectively. In each case, the molecule sits on a special position and the metal−metal bond is along the 4-fold axis. Because of static disorder, the ligands were modeled in two positions, each of occupancy ca. 50%. The structures refined well, giving acceptable residuals. All nondisordered, non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined constrained to their parent atoms.

The data for **3** were collected at 296(2) K on a Bruker SMART 1000 CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube operated at 2000 W of power. The detector was placed at a distance of 4.904 cm from the crystal. A total of 1250 frames were collected with a scan width of 0.3° in φ and an exposure time of 30 s/frame. The total data collection time was 12.8 h. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a tetragonal unit cell yielded a total of 2650 reflections to a maximum 2θ angle of 56.44° (0.73 Å resolution), 818 of which were independent (redundancy 3.23, completeness 81.40%, $R_{int} = 4.26\%$, $R_{sig} = 4.47\%$) and 630 (77.0%) of which were greater than $4\sigma(F)$. The final cell constants of $a = 10.4935(6)$ Å, $c = 14.615(1)$ Å, and $V = 1609.3(2)$ Å^3 were based upon the refinement of the *XYZ*-centroids of 1734 reflections above $20\sigma(I)$. Data were corrected for absorption effects with the SADABS program, with minimum and maximum transmission coefficients of 0.71 and 0.97, respectively. Analysis of the data showed negligible decay during data collection.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $M_2(hpp)_4Cl_2$

	M = W, **1**	M = Os, **2**	M = Pt, **3**
M(1)−M(1a)	2.250(2)	2.379(2)	2.440(1)
M(1)−Cl(1)	3.064(9)	2.667(4)	2.481(4)
M(1)−N(11)	2.08(1)	2.039(8)	1.97(1)
N(11)−M(1)−N(11a)	89.987(7)	89.96(1)	89.80(4)
N(11)−M(1)−N(11b)	178.3(6)	177.0(4)	173.2(6)
N(11)−C(17)−N(11c)	119(2)	115(1)	115(1)

The structure was solved and refined using the Bruker SHELXTL (version 5.1) software package, using the tetragonal space group *I*4222 and a racemic twinning model, with *Z* = 2 for the formula unit $C_{28}H_{48}Cl_2N_{12}Pt_2$. The final anisotropic full-matrix least-squares refinement on F^2 converged at R1 = 4.60%, wR2 = 11.70%, and a goodness-of-fit of 1.095, leaving a spurious peak on the final difference map of 5.59 e$^-$/Å^3. The structure is very similar to those of all other $M_2(hpp)_4Cl_2$ compounds. We feel that the uncertainties in the Pt−Pt and Pt−Cl bond lengths are sufficiently low as to permit meaningful comparison to other diplatinum compounds. The calculated density for $C_{28}H_{48}Cl_2N_{12}Pt_2$ is 2.092 g/cm^3, and *F*(000) is 980 e$^-$.

Crystallographic parameters are summarized in Table 1, and selected bond distances and angles are shown in Table 2. The complexes **1** and **2** are shown in Figures 1 and 2, respectively. Complex **3** is comparable to **2**. All three complexes contain a dimetal unit bridged by four hpp ligands with chloride ions in the axial positions.

Discussion

As a result of the work reported here, we now have a complete series of $M_2(hpp)_4Cl_2$ compounds for the elements W, Re, Os, Ir, and Pt. Theoretical work that will elucidate the electronic structures of these molecules is now in progress. There is, obviously, one missing element, tantalum, but all efforts to date to make $Ta_2(hpp)_4$ or $Ta_2(hpp)_4Cl_2$ have been unsuccessful.[11]

In the entire series of five compounds, the key dimensions, M−M distances and M−Cl distances, are shown in Table 3.

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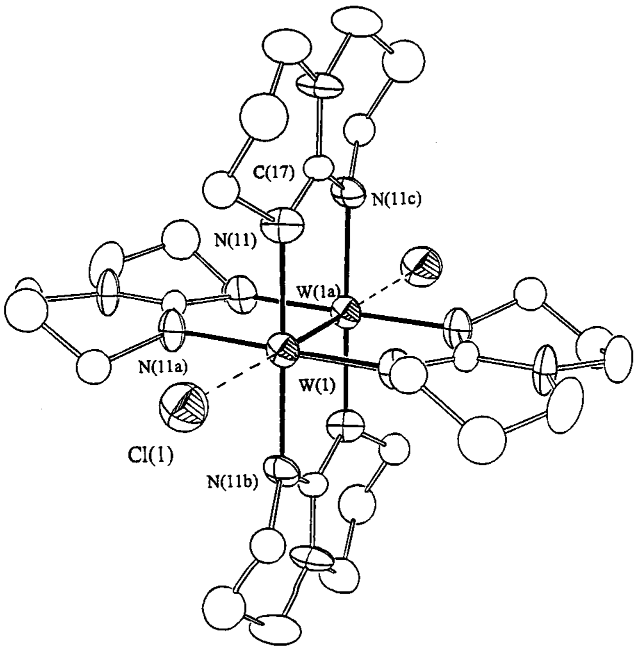

Figure 1. Molecular structure of $W_2(hpp)_4Cl_2$, **1**. Hydrogen atoms and the disordered portion of the ligands have been omitted for clarity. Displacement ellipsoids for the W, N, and Cl atoms are shown at the 50% probability level.

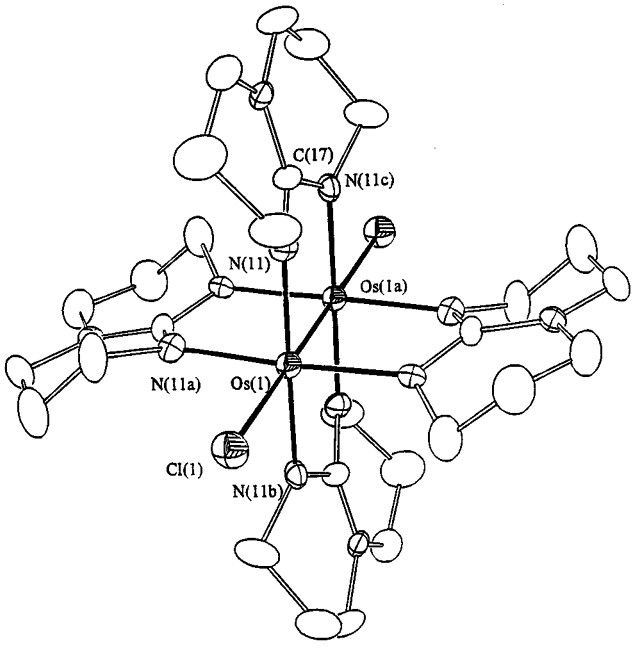

Figure 2. Molecular structure of $Os_2(hpp)_4Cl_2$, **2**. Hydrogen atoms and the disordered portion of the ligands have been omitted for clarity. Displacement ellipsoids for the W, N, and Cl atoms are shown at the 50% probability level.

Table 3. M−M and M−Cl Distances (Å) in $M_2(hpp)_4Cl_2$ Molecules

M	M−M	M−Cl	formal M−M bond order	ref
W	2.250(2)	3.064(9)	3	this work
Re	2.191(1)	2.749(5)	4	6
Os	2.379(2)	2.667(4)	3	this work
Ir	2.495(1)	2.617(4)	2	7
Pt	2.440(1)	2.481(4)	1	this work

Even a casual glance at these data reveals that the M−M distances change in an irregular fashion and the M−Cl distances, except for Pt−Cl, are so long as to imply only very weak axial bonding. It is to account for these facts that the theoretical studies mentioned above are being done. For the present, we shall discuss each of the three new compounds and compare its structure with data on related compounds of the same element.

$W_2(hpp)_4Cl_2$. The only W_2^{6+} compounds for which paddlewheel structures have previously been reported[12] are of the type $W_2(O_2CCH_3)_4R_2$, where the axial ligand is an alkyl group such as benzyl or neopentyl. The W−W distances in these range from 2.186(1) to 2.203(1) Å, which means that they are about 0.055 Å shorter than that in $W_2(hpp)_4Cl_2$, despite the strong axial interactions. The W−C distances ranged from 2.170(7) to 2.20(3) Å, whereas in $W_2(hpp)_4Cl_2$ the W−Cl distance is 3.064(9) Å. Even after allowance is made for the larger covalent radius of Cl (by 0.22 Å), this is an increase of ca. 0.65 Å. Perhaps the simplest way to reconcile these data is to propose that in each case there is a triple bond between the tungsten atoms, but of a $\pi^4\delta^2$ type in the carboxylates and a $\sigma^2\pi^4$ type in $W_2(hpp)_4Cl_2$. However, this is not obviously in accord with the relative W−W bond distances, since one might expect the $\sigma^2\pi^4$ bond to be stronger and shorter than the $\pi^4\delta^2$ bond. That is one reason further theoretical study of the compounds in this series is necessary.

There is presently no $W_2(hpp)_4$ compound with which to compare the bond distance in $W_2(hpp)_4Cl_2$, although the isolation of that compound may be possible. We can, however, make a comparison with the W−W distance[13] of 2.187(1) Å in $W_2(DtolF)_4$ (where DtolF represents $(p\text{-}CH_3C_6H_5N)_2CH^-$). Since the distance in $Mo_2(hpp)_4$ was found[3] to be shorter than that in $Mo_2(DtolF)_4$, we might estimate that the W−W distance in $W_2(hpp)_4$ would be 2.17 Å, which is 0.08 Å shorter than that in $W_2(hpp)_4Cl_2$. An increase of 0.08 Å on removal of two δ-bonding electrons is reasonable, especially when compared to the change[3] of 0.07 Å from $Mo_2(hpp)_4$ to $Mo_2(hpp)_4(BF_4)_2$. In summary, a good empirical case can be made for a $\sigma^2\pi^4$ W−W triple bond in $W_2(hpp)_4Cl_2$, and the W−W distance to be expected in $W_2(hpp)_4$, if and when it is made, should be about 2.17 Å.

$Os_2(hpp)_4Cl_2$. Molecules with the general formula $Os_2(LL)_4Cl_2$ have, as a class, been problematic. The problems arise because for the 10-electron configuration there are three possibilities: $\sigma^2\pi^4\delta^2\delta^{*2}$, $\sigma^2\pi^4\delta^2\delta^*\pi^*$, and $\sigma^2\pi^4\delta^2\pi^{*2}$, which we shall henceforth abbreviate to δ^{*2}, $\delta^*\pi^*$, and π^{*2}, respectively. For those compounds in which LL is a carboxylate, it has been concluded that the ground state (^3E_u) arises from the $\delta^*\pi^*$ configuration.[14] For the $Os_2(O_2CR)_4Cl_2$ compounds the Os−Os and Os−Cl distances are about 2.31 and 2.43 Å, respectively.

The most useful criteria for assigning ground-state configurations have been magnetic behavior and structure. In its simplest form, the magnetic criterion is based on the fact that, with a δ^{*2} configuration, there are no unpaired electrons while, for both the $\delta^*\pi^*$ and π^{*2} configurations, there must be two unpaired electrons. In the case of $Os_2(hpp)_4Cl_2$ the magnetic criterion indicates that we have a δ^{*2} configuration. The compound displays only temperature-independent paramagnetism (TIP; 4.1×10^{-5} emu/mol), as shown by the plot of magnetic susceptibility vs temperature in Figure 4. In accord with this, the ^1H NMR spectrum shows the expected three

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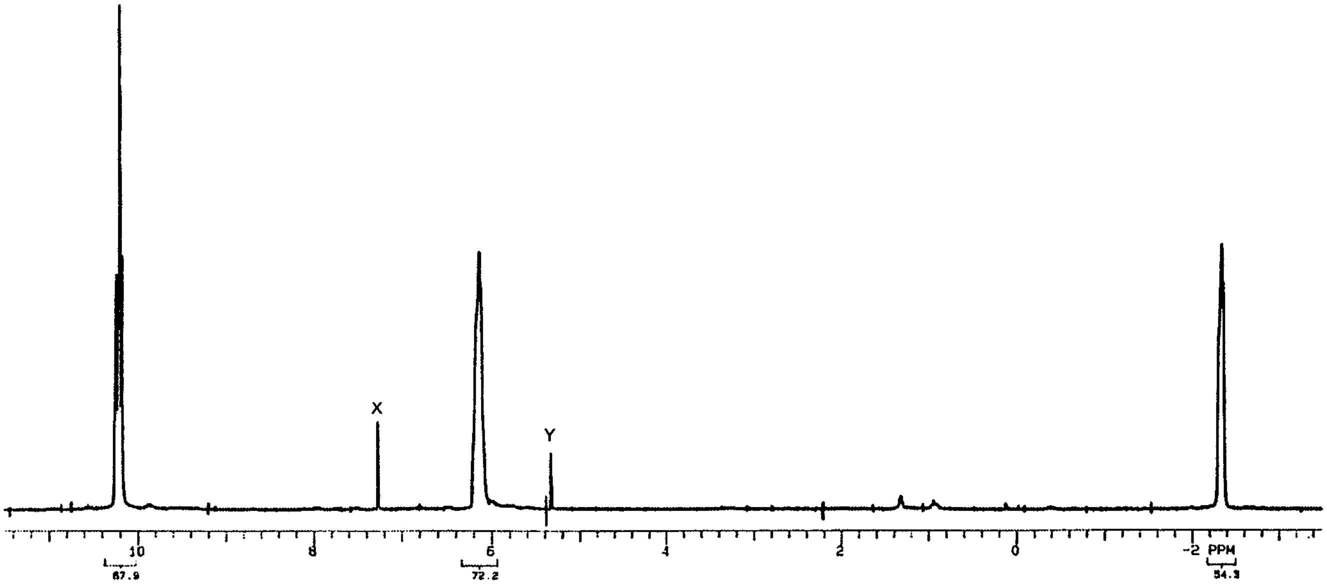

Figure 3. ^{1}H NMR spectrum of $Os_2(hpp)_4Cl_2$, **2**. In the spectrum, X indicates the $CDCl_3$ signal and Y labels the CH_2Cl_2 signal.

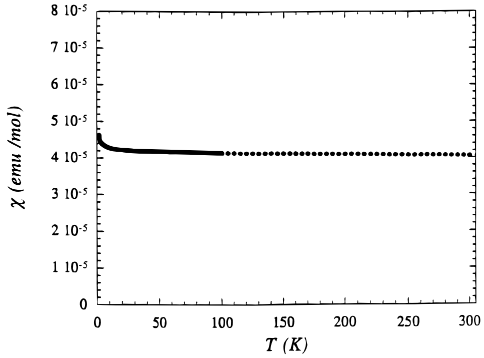

Figure 4. Temperature dependence of the magnetic susceptibility for $Os_2(hpp)_4Cl_2$, **2**. Between 2 and 10 K, a very small extrinsic paramagnetic impurity is observed which corresponds to 0.004% of spin $S = 1/2$.

methylene proton signals, but displaced upfield and downfield by the paramagnetism. A key fact is that the positions of these lines are independent of temperature between −60 and +30 °C, in accord with the TIP, whereas, if we had the much more common situation of a singlet-ground-state/triplet-excited-state Boltzmann distribution, the chemical shifts would have varied with temperature.

The structural criterion for electron configuration is based on the idea that gain or loss of a π^* electron should cause a relatively large change (ca. 0.07 Å) in the Os−Os distance while gain or loss of a δ^* electron should cause a change of only about 0.03 Å. These expectations are based on a wealth of data from many compounds containing multiple metal−metal bonds.[15] However, it must be kept in mind in applying these criteria that the actual Os−Os distances may depend also on the identity of the bridging (LL) ligand.

We previously studied the molecule $Os_2(DtolF)_4Cl_2$ in detail, both experimentally and theoretically, and established conclusively that there is a π^{*2} configuration in this case.[16] The Os−Os bond length on $Os_2(DtolF)_4Cl_2$ is 2.4672(6) Å. According to the above structural criteria, a change from a π^{*2} to a δ^{*2} configuration should lead to a shortening of $2(0.07 - 0.03) = 0.08$ Å, which is exactly the difference between the bond length in $Os_2(hpp)_4Cl_2$ (2.379(2) Å) and that in $Os_2(DtolF)_4Cl_2$. This seemingly perfect agreement should not be taken too seriously since the bridging ligands have been changed and there is also a change in the Os−Cl distance of about 0.2 Å. However, the structural data are certainly in satisfactory accord with the proposed electron configurations.

$Pt_2(hpp)_4Cl_2$. Apart from long-known diplatinum(III) compounds with bridging sulfate and phosphate groups,[17] there are only two previously known compounds that are comparable with this one. In $Pt_2(DPhF)_4Cl_2$, the Pt−Pt bond length[18] is 2.517(1) Å and the Pt−Cl bond length is 2.424(3) Å. Thus, as has often been the case, the hpp ligand gives a shorter M−M distance (in this case much shorter, 2.440(1) Å) than the formamidinate ligand, while the Pt−Cl distance is somewhat longer, at 2.481(4) Å. In both of these cases the Pt−Pt distances are longer than that in the $[Pt_2(O_2CCH_3)_4(H_2O)_2]^{2+}$ ion,[19] where it is 2.391(1) Å. Despite these small variations, it seems clear that there is, in each case, a Pt−Pt single bond but also fairly close attachment of the axial ligands.

Acknowledgment. We thank the National Science Foundation for financial support and the Bruker Analytical X-ray Systems Corp. of Madison, WI, for collecting the X-ray data used for the solution and refinement of the $Pt_2(hpp)_4Cl_2$ structure.

Supporting Information Available: X-ray crystallographic files, in CIF format, for **1**, **2**·$4CH_2Cl_2$, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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