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The First Structurally Confirmed Paddlewheel Compound with an M_2^{7+} Core: $[Os_2(hpp)_4Cl_2](PF_6)$

F. Albert Cotton,*,[†] Naresh S. Dalal,[‡] Penglin Huang,[†] Carlos A. Murillo,*,[†] Ashley C. Stowe,[‡] and Xiaoping Wang[†]

Department of Chemistry and Laboratory for Molecular Structure and Bonding, P.O. Box 30012, Texas A&M University, College Station, Texas 77842-3012, and Department of Chemistry and Biochemistry, and Center for Magnetic Resonance, National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32306-4390

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Oxidation of $Os_2(hpp)_4Cl_2$, **1** (hpp = the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine), with $(FeCp_2)PF_6$ produces air-stable $[Os_2(hpp)_4Cl_2]PF_6$, **2**. This is the first structurally confirmed metal–metal bonded paddlewheel compound having an M_2^{7+} core. The Os–Os distances for two crystalline forms, **2**·2acetone and **2**·hexane, are 2.3309(4) and 2.3290(6) Å, respectively. EPR, ^{1}H NMR, and magnetization data indicate that **2** has an unpaired electron and an exceptionally low *g* value of 0.791 ± 0.037. An electrochemical study shows that there is a quasireversible wave corresponding to a more highly oxidized species with an unprecedented Os_2^{8+} core.

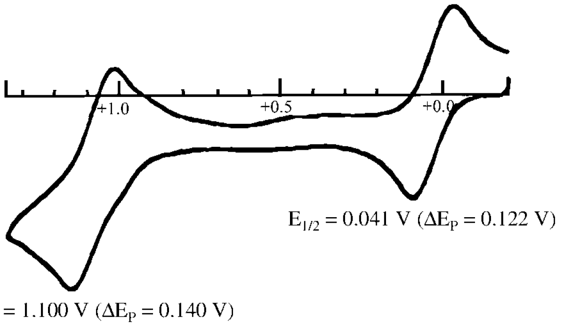

Figure 1. Cyclic voltammogram of $Os_2(hpp)_4Cl_2$ (175 mV/s) in CH_2Cl_2 referenced to Ag/AgCl. The supporting electrolyte was $(Bu_4N)PF_6$ (0.1 M).

In recent years compounds of the types $M_2(hpp)_4Cl_n$, where hpp is the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine, $n = 0$, 1, or 2 and M = V,[1] Cr,[1] Mo,[1,2] Nb,[3] W,[4,5] Os,[4] Pt,[4] Re,[6] Ru,[7] Ir,[8] and Pd,[9] have been reported. This and other work[2b] has shown that the guanidinate-type hpp ligand has an exceptional ability to stabilize M_2^{n+} cores in high oxidation states. This tendency is so strong that it causes $W_2(hpp)_4$ to ionize more readily than cesium.[10] In the 40 years during which M_2^{n+} compounds of most transition metals have been studied, and well over 3000 have been reported, not one has ever been isolated with an M_2^{7+} core. There has been a tendency to assume that with this high a charge the metal atom orbitals would be too contracted to give sufficient overlap to sustain M−M bonding. In the case of $Os_2(hpp)_4Cl_2$ the cyclic voltammogram in CH_2Cl_2 (Figure 1) shows that a *reversible* one-electron oxidation is readily accessible (0.041 V vs Ag/AgCl).[11] The second oxidation wave centered at 1.100 V corresponds to an unprecedented $Os_2(hpp)_4^{4+}$ species. The assignment of these processes as oxidation steps became unambiguous when the mild one-electron oxidant $(FeCp_2)PF_6$ was successfully used to prepare the $Os_2(hpp)_4^{3+}$ species (see below). When the voltammogram was measured in THF, a reduction wave appeared at −1.405 V.[12] For this reason, we undertook the work reported here, which has led to the isolation and characterization of the first paddlewheel compound with an

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* Authors to whom correspondence should be addressed. E-mail: cotton@tamu.edu (F.A.C.); murillo@tamu.edu (C.A.M.).

[†] Texas A&M University.

[‡] Florida State University.

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(11) Under the same conditions the $FeCp_2/FeCp_2^+$ couple appears at 0.533 V.

(12) Under these conditions, the $FeCp_2/FeCp_2^+$ couple appeared at 0.560 V and the other two oxidation waves at 0.085 and 1.050 V.

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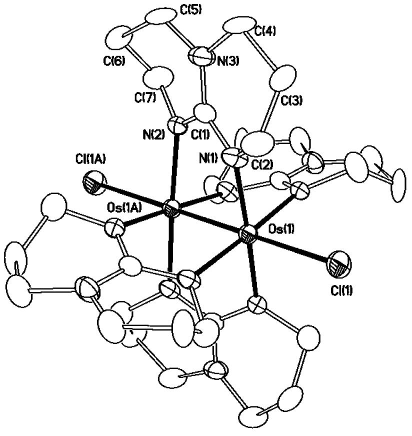

Figure 2. Perspective view of one orientation of the $Os_2(hpp)_4Cl_2^+$ cation in **2**·hexane. Atoms are drawn with ellipsoids at their 40% probability level. Hydrogen atoms are omitted for clarity.

M_2^{7+} core.[13] Efforts are being made to isolate the more highly oxidized species.

Preparation of the title compound was accomplished by treating air-sensitive solutions of the previously reported Os_2^{6+} compound,[4] $Os_2(hpp)_4Cl_2$, **1**, with $(FeCp_2)PF_6$, in CH_2Cl_2,[14] whereby air-stable $[Os_2(hpp)_4Cl_2](PF_6)$, **2**, was obtained. The structure of this compound has been determined as two different solvates,[15] and the structure of the cation is shown in Figure 2. The dimensions of the neutral molecule and the cation are listed and compared in Table 1.

The major changes are in the lengths of the Os−Os and Os−Cl distances, but since the overall structures do not differ significantly, the reversibility of the electrochemistry is understandable. However, even the small structural changes are highly significant in terms of bonding. It was previously concluded that **1**, which displays only temperature-independent paramagnetism (tip), has a ground state based on the $\sigma^2\pi^4\delta^2\delta^{*2}$ electron configuration, and it is difficult to see any other plausible ground state configuration. Thus it would be expected that **2** would be well described by a $\sigma^2\pi^4\delta^2\delta^*$ configuration, although the $\sigma^2\pi^4\delta^2\pi^*$ configuration might also be considered. Interestingly, removal of one electron from an antibonding orbital decreases the Os−Os bond distance by ca. 0.05 Å. The magnitude of the change is similar to that of the couple $Re_2Cl_4(PMe_3)_4$/$[Re_2Cl_4(PMe_3)_4]ReO_4$,[16] where the former has a bond order of 3 and an electronic configuration of $\sigma^2\pi^4\delta^2\delta^{*2}$ and the oxidized species has a bond order of 3.5 and a $\sigma^2\pi^4\delta^2\delta^*$ electronic configuration. In this couple the Re−Re bond distance decreases from 2.247(1) to 2.205(1) Å upon oxidation. The change in metal−metal distance is also similar to that found in the two $M_2(hpp)_4^{n+}$ series where M = Mo,[2a] W[5] and n = 0, 1, 2. It is somewhat surprising, however, that the magnitude of the change in Os−Os distance is so constant for these highly oxidized species since the increase in the internuclear charge would be expected to increase the intermetal repulsion and thus offset the effect of the removal of the antibonding electron.[17] It is likely that the strong basicity of the hpp ligand is responsible for this effect.[2a,18] Also, for the Os_2^{6+} compounds the Os−Cl distances are long and decrease as the oxidation state of the metal atom increases as expected by the increase of the electrostatic attraction.[19]

Table 1. Comparison of the Core Distances (Å)[a]

	1·4CH$_2$Cl$_2$	**2**·2acetone	**2**·hexane
Os−Os	2.379(2)	2.3309(4)	2.3290(6)
Os−Cl	2.667(4)	2.520(1)	2.543(2)
Os−N$_{av}$	2.039(8)	2.042[8]	2.045[7]

[a] Numbers in square brackets represent averaged numbers.

The ^1H NMR spectrum of **2**·2acetone in CD_2Cl_2 solution shows three broad bands for the hpp ligands centered at δ values of 16.90, 3.60, and −0.85 ppm that integrate in the approximate ratio 1:1:1. The acetone signal appears at 2.12 ppm.[20] The broadness and the significant shifts of the signals are in agreement with the presence of a paramagnetic species. Furthermore, magnetic data obtained at room temperature using the Evans method,[21] a SQUID magnetometer, and a magnetic susceptibility balance gave values of $\chi_M T$ in the range 0.201−0.244 emu K/mol corresponding to values of μ_{eff} (μ_B) of 1.27−1.39 at room temperature. At low

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(13) There are two such species that have been presumed to exist from electrochemical data, viz., $[Ru_2(hpp)_4Cl_2]^+$ and $[Ru_2(corrole)_2]^+$, but not isolated. For $[Ru_2(corrole)_2]^+$ see: Kadish, K. M.; Burdet, F.; Jérôme, F.; Barbe, J.-M.; Ou, Z.; Shao, J.; Guilard, R. *J. Organomet. Chem.* **2002**, *652*, 69.

(14) To a mixture of $Os_2(hpp)_4Cl_2$ (415 mg, 0.413 mmol) and $(FeCp_2)PF_6$ (137 mg, 0.414 mmol) was added 20 mL of CH_2Cl_2. A deep purple color appeared immediately. The mixture was stirred for 1 h at room temperature and then filtered into a Schlenk tube. A small amount of brown solid residue was discarded, leaving a deep purple solution. The solvent was removed under vacuum, leaving a dark solid, which was washed with 2 × 30 mL of ether, then dissolved in 15 mL of acetone, and layered with 30 mL of hexanes. Dark block-shaped crystals of **2**·2acetone were obtained within 3 days. Yield: 449 mg, 86%. Crystals of **2**·hexane were obtained by dissolving purple crystals of **2** in dichloroethane and then layering the solution in hexanes. For physical characterizations, the crystalline sample was crushed and pumped under vacuum overnight to remove cocrystallizing solvent. IR (cm^{-1}, KBr): 2940(m), 2865(m), 1655(w), 1543(s), 1468(m), 1383(m), 1312(m), 1217(m), 1133(m), 1031(w), 840(s), 763(m), 557(w). Anal. Calcd for $C_{28}H_{48}N_{12}Os_2Cl_2PF_6$: C, 29.27; H, 4.21; N, 14.63. Found: C, 29.62; H, 4.24; N, 14.39. UV−vis (CH_2Cl_2): 369 nm, ϵ = 20300 L mol^{-1} cm^{-1}; 536 nm (vbr), ϵ = 20000 L mol^{-1} cm^{-1}.

(15) (a) Crystallographic data for **2**·hexane: $C_{34}H_{62}Cl_2F_6N_{12}Os_2P$, tetragonal, space group *P*4/*mbm*, $a = 13.2645(8)$ Å, $c = 12.3852(7)$ Å, $V = 2179.1(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.883$ g cm^{-3}. $T = 213$ K. R1 = 0.0331, wR2 = 0.0746, GOF = 1.030 for all data. (b) Crystallographic data for **2**·2acetone: $C_{34}H_{60}Cl_2F_6N_{12}O_2Os_2P$, orthorhombic, space group *Pnma*, $a = 17.282(2)$ Å, $b = 25.425(2)$ Å, $c = 10.1454(9)$ Å, $V = 4457.9(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.885$ g cm^{-3}. $T = 213$ K. R1 = 0.0442, wR2 = 0.0739, GOF = 1.169 for all data.

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(17) Such effects have been observed as Re_2^{5+} units are oxidized to the quadruple-bonded Re_2^{6+} units. See, for example: Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Tomas, M.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 4950.

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(19) This effect is reflected also in an increase in the intensity of the electronic absorption coefficients. The ϵ values for the bands in **2** are ca. 20000 L mol^{-1}cm^{-1} (see ref 14) while those in **1** are 10900, 7600, and 7670 L mol^{-1} cm^{-1} for the bands at 355, 465, and 495 nm, respectively. For **1** there is also a weak shoulder at 585 nm (see ref 4).

(20) In the ^1H NMR there is also a peak at 1.54 ppm due to water present in commercial CD_2Cl_2 (see Supporting Information).

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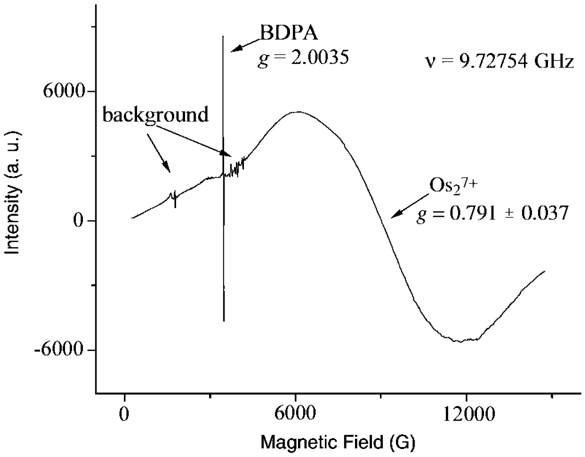

Figure 3. A first-derivative X-band EPR spectrum of **2** at 6.5 K.

temperature these values drop significantly, presumably because of the strong spin−orbit coupling of the Os atoms. The room temperature values are consistent with the presence of one unpaired electron. This conclusion is also supported by the observation of a strong EPR signal from a crystalline powder of **2** from 77 to 4 K (Figure 3). The observed *g* value of 0.791 ± 0.037 can thus be assigned to the unpaired electron on the cation of **2**. The observed peak-to-peak line width (∼6000 G) is exceptionally large, and can be contrasted with the sharpness of the signal from the free radical α,γ-bisdiphenylene-β-phenylallyl (BDPA) at $g = 2.0035$. While further theoretical work is needed to understand the origin of the markedly low *g* value and the quite unusual peak width, both can be qualitatively ascribed to the very large spin−orbit coupling in the Os ion. For comparison, the calculated value of λ for Os^{3+} is $\sim$3000 cm^{-1} and that for Os^{5+} is $\sim$4500 cm^{-1}. The latter is among the largest reported values.[22] It should be noted that *g* values for Os complexes are very sensitive to structure and bonding, and these have been reported over a wide range.[23]

In conclusion, **2** represents the first structurally confirmed paddlewheel compound with an M_2^{7+} core. The bond order can be assigned as 3.5. As expected, the magnetic measurements confirm the presence of an unpaired electron. The stability of M_2^{7+} and M_2^{8+} cores, despite the tendency for M−M bonding to be adversely affected by contraction of the metal atom, d orbitals that give rise to the σ and π bonding, may be attainable only with supporting ligands of exceptionally high basicity such as hpp. The unusually low *g* value of 0.79 and the exceptionally large EPR line width should stimulate further theoretical and experimental investigations.

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Supporting Information Available: The ^1H NMR spectrum of **2**·2acetone in CD_2Cl_2 and variable temperature magnetic data for **2** in PDF and the X-ray crystallographic data in CIF format for **2**·2acetone and **2**·hexane. This material is available free of charge via the Internet at http://pubs.acs.org.

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