COMMUNICATION

Dalton
www.rsc.org/dalton

A highly oxidized Re_2^{7+} species with an electron-poor bond of order 3.5

John F. Berry, F. Albert Cotton,* Penglin Huang and Carlos A. Murillo*

Department of Chemistry and Laboratory for Molecular Structure and Bonding,
PO Box 30012 Texas A&M University, College Station, Texas 77842-3012, USA.
E-mail: cotton@tamu.edu (F.A.C.); murillo@tamu.edu (C.A.M.)

Received 4th February 2003, Accepted 24th February 2003
First published as an Advance Article on the web 4th March 2003

The first paddlewheel complex with an Re_2^{7+} core and an electron-poor bond order of 3.5 is paramagnetic and shows a metal–metal bond lengthening of 0.035 Å relative to the corresponding compound having a quadruple bond and an Re_2^{6+} core.

Nearly forty years ago, the deliberate study of compounds with multiply-bonded dimetal cores in tetragonal coordination environments (*e.g.*, Fig. 1a,b) began with the correct identification of the stoichiometry, as well as the geometric and electronic structures (especially the last) of the $Re_2Cl_8^{2-}$ ion.[1–4] The field has since grown to embrace more than three thousand compounds of all the d-block transition metals except, as yet, those of group 3, tantalum and manganese.[5] Among these many compounds formal oxidation states of the cores (*i.e.*, values of n in M_2^{n+}) have been limited to a range from +4 to +6. Research in this laboratory has been directed toward widening this range. To this end we have very recently prepared paddlewheel compounds containing V_2^{3+} and Os_2^{7+} cores.[6,7]

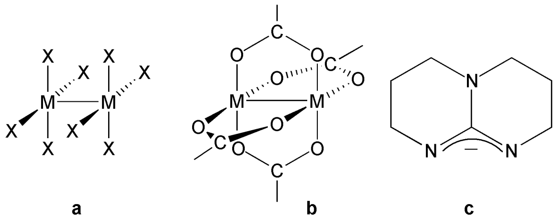


Fig. 1 Two multiply-bonded dimetal cores in tetragonal environments (a, b) and a line drawing of the hpp ligand (c).

For the Re_2^{n+} compounds, the range of n has been 4, 5 and 6 which correspond to bond orders of 3, 3.5 and 4, respectively, the first two being of the electron rich variety.[5] These are among the most widely studied metal–metal bonded compounds but so far a multitude of electrochemical studies have failed to turn up evidence for stable Re_2^{n+} species outside the range Re_2^{4+} to Re_2^{6+}. We now report that it is possible to isolate as well as structurally, and in other ways, characterize a thermodynamically stable compound containing an Re_2^{7+} core. This has been done by taking advantage of the demonstrated exceptional capacity of the hpp ligand (hpp = the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido-[1,2*a*]pyrimidine) (Fig. 1c) to stabilize higher oxidation states of M_2^{n+} units.[8] The new compound $[Re_2(hpp)_4Cl_2]PF_6$, **1**, was prepared† by the reaction of $Re_2(hpp)_4Cl_2$[9] with one equivalent of $(FeCp_2)PF_6$ in CH_2Cl_2. After extraction with acetone and layering with hexanes, crystals of **1**·2acetone were obtained. The structure of the cation, as determined by X-ray crystallography,‡ is shown in Fig. 2.

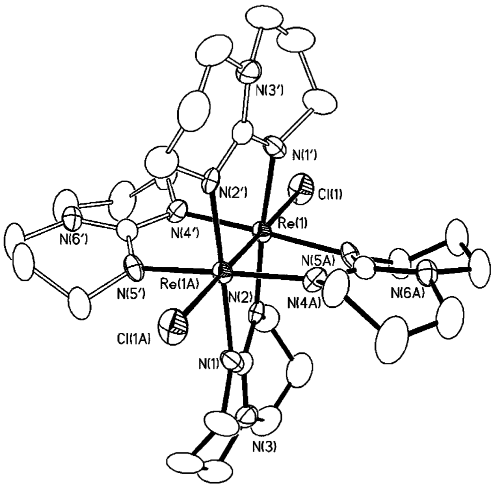
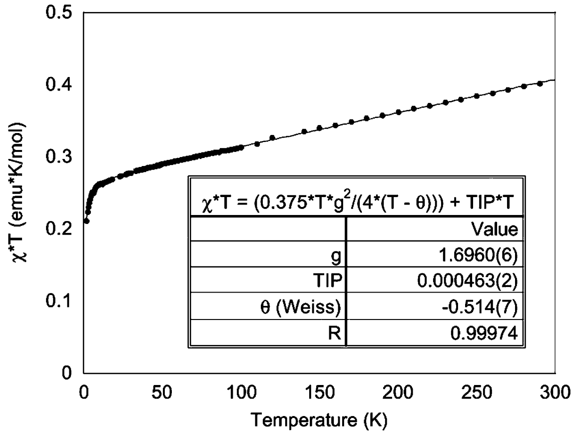


Fig. 2 A perspective view of one of the orientations of the $Re_2(hpp)_4Cl_2^+$ cation in **1**·2acetone showing the puckering of the hpp rings. Selected distances are: Re(1)–Re(1A), 2.2241(4); Re(1) ··· Cl(1), 2.613(1); Re(1)–N(1′), 2.069(4); Re(1)–N(2), 2.066(4); Re(1)–N(4′), 2.071(4) Å. Ellipsoids are drawn at the 40% probability level and all hydrogen atoms are omitted.

Even with the highly oxidized core, the major properties of the cation are correctly predicted by our general understanding of the chemical bonding in M_2^{n+} species.[10] We expect that an electron removed from $Re_2(hpp)_4Cl_2$ would come from a δ-bonding orbital; its loss would lower the Re–Re bond order from 4 to 3.5. In accord with this (as well as with the fact that the overall increased charge on the Re_2 unit will contract the 5d orbitals and thus diminish the σ and π overlaps)[11] we would expect a lengthening of the Re–Re bond length by 0.03–0.05 Å. The value found is 0.035 Å. The Re–Re bond in this Re_2^{7+} species corresponds to an electron-poor electronic configuration of bond order 3.5, in contrast to the electron-rich bonds, *i.e.*, those having the same bond order but electron-rich Re_2^{5+} cores. The presence of one unpaired electron in $[Re_2(hpp)_4Cl_2]^+$ was established by magnetic measurements,§ Fig. 3 and by an EPR spectrum of the compound in a frozen THF glass.

The cyclic voltammogram of the precursor $Re_2(hpp)_4Cl_2$ in CH_2Cl_2 is shown in Fig. 4. It has waves centered at $E_{½}$ of 58 and



$\chi*T = (0.375*T*g^2/(4*(T - \theta))) + TIP*T$

	Value
g	1.6960(6)
TIP	0.000463(2)
θ (Weiss)	-0.514(7)
R	0.99974

Fig. 3 Magnetic susceptibility measurements of **1**. The $\chi_M T$ values are in emu K mol^{-1}. The solid line represents the theoretical fit of the data using the equation given in the inset.

DOI: 10.1039/b301360j

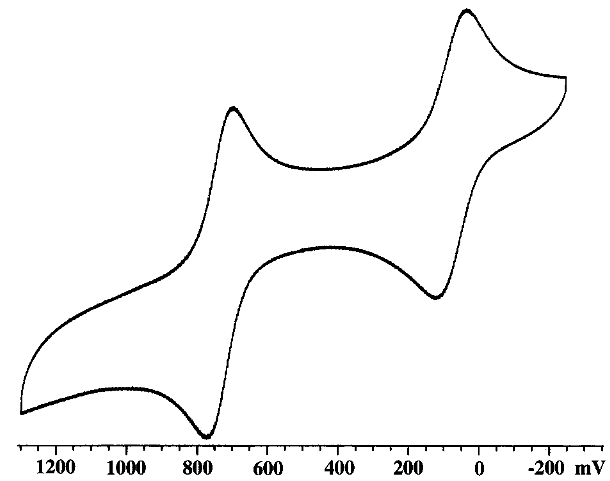


Fig. 4 Cyclic voltammogram of the precursor, $Re_2(hpp)_4Cl_2$ (200 mV s^{-1}), in CH_2Cl_2 referenced to Ag/AgCl using 0.1 M Bu_4NPF_6 as supporting electrolyte. The $E_{½}$s are 733 and 58 mV. Under similar conditions the $E_{½}$ for the Fc/Fc^+ couple appeared at 440 mV.

733 mV (*vs.* Ag/AgCl). Since the $E_{½}$ of the ferrocene/ferrocenium couple is 440 mV under similar conditions, the successful oxidation of $Re_2(hpp)_4Cl_2$ with $(FeCp_2)PF_6$ clearly indicates that the wave centered at 58 mV corresponds to a first oxidation to $Re_2(hpp)_4Cl_2^+$. Consequently, the other wave must be a second oxidation and there may well be an isolable $Re_2(hpp)_4Cl_2^{2+}$ ion. Efforts are being made to isolate it in a stable form.

As we recently reported[12] for $W_2(hpp)_4$, among the reasons why hpp can so effectively stabilize higher oxidation states of M_2 cores is that there are strong and complex interactions between the δ and δ* orbitals of the M_2^{n+} core and the symmetry-matched combinations of hpp π-orbitals. One of the consequences of this is that it is no longer possible to neatly identify a unique, metal-centered δ ⟶ δ* transition in the visible or near-IR spectrum. Thus, we cannot make any statement about that here. The spectra of both $Re_2(hpp)_4Cl_2$ and $[Re_2(hpp)_4Cl_2]^+$ show several low-energy absorptions, as shown Fig. 5. The notion of "innocent" ligands (those that are only, or little more than, electron pair donors) and "non-innocent" ligands (those that have other important overlaps with metal orbitals) which is well recognized in classical (*i.e.*, one-center) coordination chemistry is equally appropriate to the chemistry of M_2^{n+} cores. Thus, while $Re_2Cl_8^{1-}$ cannot be obtained from $Re_2Cl_8^{2-}$ since Cl is a (relatively) innocent ligand, hpp is distinctly non-innocent and opens new possibilities, including not only the Re_2^{7+} core which is now well-characterized, but (at least electrochemically) the Re_2^{8+} core which we hope to isolate in a $[Re_2(hpp)_4Cl_2]^{2+}$ compound.

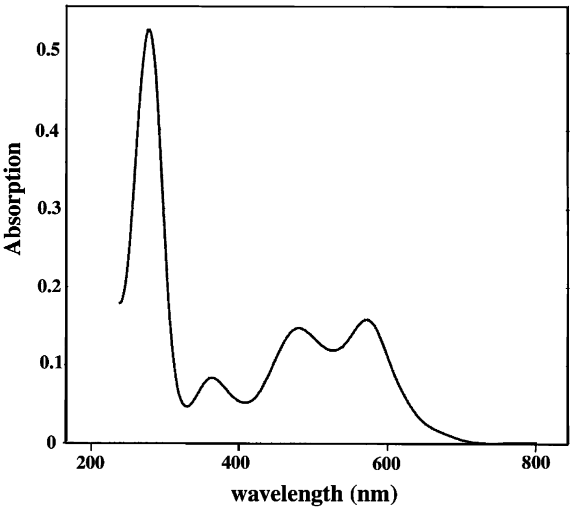


Fig. 5 The electronic spectrum of **1** in CH_2Cl_2. The bands at 276, 361, 478 and 570 nm have ε of 37700, 5970, 10500 and 11300 L mol^{-1} cm^{-1}, respectively. All these ε values are too high to be assigned to a simple metal-centered δ ⟶ δ* transition.

We thank C. S. Fewox for help with EPR measurements and gratefully acknowledge support from the National Science Foundation through a Nanoscale Science and Engineering/NIRT Grant (DMR-0103455); from Texas A&M University through the Laboratory for Molecular Structure and Bonding; and from the Robert A. Welch Foundation (Grant No. A494). J. F. B. thanks the National Science Foundation for support in the form of a predoctoral fellowship.

Notes and references

† Synthesis of $[Re_2(hpp)_4Cl_2]PF_6$. Purple $Re_2(hpp)_4Cl_2$ (409 mg, 0.411 mmol) and $(FeCp_2)PF_6$ (136 mg, 0.411 mmol) were mixed together, and 20 mL of CH_2Cl_2 was added. A pinkish red color appeared immediately, and the solids dissolved. The mixture was stirred at room temperature for 2 h. The solvent was removed under vacuum, leaving a dark solid, which was further washed with 2 × 20 mL of ether. The washing was yellow. The remaining solid was pumped dry and extracted with 10 mL of acetone, then filtered. The dark red filtrate was layered with 40 mL of hexanes. A brown solid that remained on the frit was discarded. X-Ray quality crystals of $Re_2(hpp)_4Cl_2]PF_6$·2acetone grew within 3 days. Yield: 300 mg, 64%. UV-Vis (CH_2Cl_2): 276 nm, ε = 37700 L mol^{-1} cm^{-1}; 361 nm, ε = 5970 L mol^{-1} cm^{-1}; 478 nm, ε = 10500 L mol^{-1} cm^{-1}; 570 nm, ε = 11300 L mol^{-1} cm^{-1}. IR (cm^{-1}, KBr): 2963 (m), 2864 (w), 1655 (w), 1637 (w), 1544 (m), 1459 (w), 1442 (w), 1404 (w), 1383 (m), 1313 (m), 1262 (s), 1217 (m), 1094 (vs), 1024 (vs), 801 (vs), 758 (m), 704 (w), 555 (w), 469 (w). Anal. calc. for $C_{28}H_{48}N_{12}Re_2Cl_2PF_6$: C, 29.47; H, 4.24; N, 14.73. Found: C, 29.60; H, 4.24; N, 14.47%.

‡ Crystal data for **1**·2acetone. M = 1257.21, orthorhombic, space group *Pnma* (no. 62), a = 17.286(1), b = 25.521(2), c = 10.1120(7) Å, V = 4461.0(6) $Å^3$, T = 213(2) K, Z = 4, D_c = 1.872 g cm^{-3}, μ(Mo-Kα) = 5.649 mm^{-1}, $R1$ = 0.0455 and $wR2$ = 0.0763 for all data. CCDC reference number 200385. See http://www.rsc.org/suppdata/dt/b3/b301360j/ for crystallographic data in CIF or other electronic format.

§ The variable temperature magnetic susceptibility data were gathered on a Quantum Design SQUID magnetometer MPMS-XL. The data were corrected for diamagnetism and fitted by using a modified Curie–Weiss equation. The major modification was inclusion of the TIP parameter, which accounts for the positive slope of the data points above 10 K. The large (~500 × 10^{-6} emu mol^{-1}) TIP parameter arises from spin–orbit coupling. Below 10 K, the χT value drops sharply. This can be accounted for by a Weiss constant of −0.5 K.

1 F. A. Cotton, N. F. Curtis, C. B. Harris, B. F. G. Johnson, S. J. Lippard, J. T. Mague, W. R. Robinson and J. S. Wood, *Science*, 1964, **145**, 1305.
2 F. A. Cotton, N. F. Curtis, B. F. G. Johnson and W. R. Robinson, *Inorg. Chem.*, 1965, **4**, 326.
3 F. A. Cotton and C. B. Harris, *Inorg. Chem.*, 1965, **4**, 330.
4 F. A. Cotton, *Inorg. Chem.*, 1965, **4**, 334.
5 F. A. Cotton and R. A. Walton, *Multiple Bonds between Metal Atoms*, 2nd edn., Oxford University Press, New York, 1993.
6 F. A. Cotton, E. A. Hillard and C. A. Murillo, *J. Am. Chem. Soc.*, 2003, **125**, 2026.
7 F. A. Cotton, N. S. Dalal, P. Huang, C. A. Murillo, A. C. Stowe and X. Wang, *Inorg. Chem.*, 2003, **42**, 670.
8 F. A. Cotton, L. M. Daniels, C. A. Murillo, D. J. Timmons and C. C. Wilkinson, *J. Am. Chem. Soc.*, 2002, **124**, 9249.
9 F. A. Cotton, J. Gu and D. J. Timmons, *J. Chem. Soc., Dalton Trans.*, 1999, 3741.
10 Ref. 5, chapter 10.
11 M. J. Bennett, F. A. Cotton and R. A. Walton, *Proc. R. Soc. London, A*, 1968, **303**, 175.
12 F. A. Cotton, N. E. Gruhn, J. Gu, P. Huang, D. L. Lichtenberger, C. A. Murillo, L. O. Van Dorn and C. C. Wilkinson, *Science*, 2002, **298**, 1971.