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First paddlewheel complex with a doubly-bonded Ir_2^{6+} core

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Reaction of $IrCl_3$ with Hhpp in refluxing ethanol (Hhpp = 1,3,4,6,7,8-hexahydro-2*H*-pyramido[1,2-*a*]pyrimidine) yields $Ir_2(hpp)_4Cl_2$, the first paddlewheel complex of Ir^{III}, with a short Ir–Ir distance of 2.495(1) Å, an average Ir–Cl distance of 2.643[6] Å, an Ir_2^{6+} core bridged by four hpp ligands with two axial chlorine atoms, and a double bond between the Ir atoms.

A great deal of understanding has come in the area of multiple bonds between transition metal atoms through the study of dinuclear paddlewheel-type complexes; however, there is very little depth to our knowledge for iridium. Indeed, there is only one paddlewheel complex containing an Ir_2^{4+} core and four bridging anionic ligands, namely $Ir_2(DTolF)_4$ (DTolF = *N*,*N*′-di-*p*-tolylformamidinate) **I**,[1] and the three-step synthesis of this was quite cumbersome. It appears that there are only seven other complexes containing a single bond between divalent iridium atoms that fall within the family of compounds broadly defined by **II**.[1,2]

Dinuclear complexes of iridium(III) are typically edge-sharing or face-sharing bioctahedra and have no metal–metal bonds because of the closed t_{2g}^6 configuration. There are a few complexes in which the short Ir–Ir bond distance is indicative of direct metal–metal bonding, *e.g.* $[Ir_2(\mu\text{-}H)_3H_2(PPh_3)_4]PF_6$,[3] 2.518 Å; $[(Cp^*Ir)_2(\mu\text{-}H)_3]ClO_4$,[4] 2.465 Å, but the close approach may be due to the $(\mu\text{-}H)_3$ bridging. No complex of the paddlewheel type has been reported for trivalent iridium.

It has been shown recently that bridging hpp, the monoanion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine, stabilizes complexes of the type $M_2(hpp)_4$ (M = V,[5] Nb,[6] Cr,[5] Mo,[5] Ni,[7] and Pd[8]). Additionally, complexes containing an M_2^{6+} core have been made for M = Ru,[9] Re,[10] Mo,[11] and Pd.[8] The complex $[Mo_2(hpp)_4][BF_4]_2$ [11] is the sole example of an Mo_2^{6+} core supported by soft, binitrogen-donor ligands as the bridges and $Pd_2(hpp)_4Cl_2$ [8] is the only example of a single bond between trivalent palladium atoms. As a result, our interest has turned more towards the +3 oxidation state of the transition metals.

For many transition metals (*e.g.* Cr, Co, Ni, Pd, Ru, Rh), simple halide salts are often used as starting materials for the synthesis of a wide variety of paddlewheel complexes, but there is no general pathway for the analogous iridium complexes. Rhenium and osmium paddlewheel complexes are typically synthesized by ligand exchange using $Re_2Cl_8^{2-}$ and $Os_2(O_2CCH_3)_4Cl_2$, respectively, but no similar diiridium starting materials are available. However, one osmium complex, $Os_2(hydroxypyridinato)_4Cl_2$, was synthesized from $OsCl_3$ and the neutral ligand in refluxing ethanol.[12] This same method was tried with $IrCl_3$ and Hhpp and resulted in only the second example of an iridium paddlewheel complex and the first one containing Ir^{III}.

When $IrCl_3$ and Hhpp were stirred in ethanol at room temperature for several hours, no reaction occurred, but heating to reflux overnight resulted in a brown solution containing a small amount of solid.† Removal of the ethanol under reduced pressure left a brown residue, which was dissolved in a minimum amount of CH_2Cl_2. From this solution a dark purple band containing $Ir_2(hpp)_4Cl_2$ **1** (10% yield) was eluted first on a silica gel column with a 10 : 1 CH_2Cl_2–MeOH eluent. Crystals can be readily grown in air by evaporation or diffusion of hexanes into a dichloromethane solution. The solid is air stable and is not decomposed by water, in which it is sparingly soluble.

When an analogous reaction was conducted in toluene, the hot toluene became purple and a dark solid precipitated. Complex **1** was isolated from the toluene filtrate by evaporation. After washing with acetonitrile the yield was reproducibly *ca.* 10%. The dark solid is as yet uncharacterized.

Substitutions in low spin d^6 systems are known to be difficult,[13] and $IrCl_3$ is no exception; this may account for the low yields of $Ir_2(hpp)_4Cl_2$. Additionally it appears that $IrCl_3$ does not react at all with Li(hpp) in refluxing THF or CH_2Cl_2. It is possible that the conditions necessary to activate these reactions also lead to several side products. Clearly a more reactive starting material is desirable, but we have not found one yet as the number of suitable Ir^{III} complexes is rather small.

The structure‡ of **1**, a diiridium unit bridged by four hpp ligands with chlorine atoms bound in the axial positions, is shown in Fig. 1. The Ir–Ir *double* bond distance is 2.495(1) Å and the average Ir–Cl bond distance is 2.643[6] Å. There is no analog with which to make a comparison. The ‘nearest kin’ is $Ir_2(DTolF)_4$ which contain an Ir_2^{4+} core and a formal Ir–Ir *single* bond of length 2.524(3) Å,[1] a relatively small change of 0.029 Å from the metal–metal distance in **1**.

Compound **1** is paramagnetic with a room-temperature magnetic susceptibility that corresponds to two unpaired electrons. This observation could be accommodated on the basis of the classic molecular orbital ordering, $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$. However, this is not necessarily the case. We recently reported[8] that $Pd_2(hpp)_4Cl$, which has two more electrons, has the configuration $\pi^4\delta^2\delta^{*2}\pi^{*4}\sigma^2$; the high energy of the σ orbital is traced to the very strong and short Pd–Cl bonds [2.474(4) Å]. In **1**, the Ir–Cl bond lengths are much longer [2.617(4) Å] and therefore the σ orbital will likely be lower in energy, although not necessarily at the bottom. However, as long as the σ orbital is below the π* orbitals, its actual position is not critical and the electronic configuraion of **1** will correspond to a net bond order of 2.

This work suggests several interesting ideas, such as reduction of the Ir_2^{6+} core to Ir_2^{4+} and the question of whether $Rh_2(hpp)_4Cl_2$ as well as $Rh_2(hpp)_4$ can be made. We are pursuing these matters.

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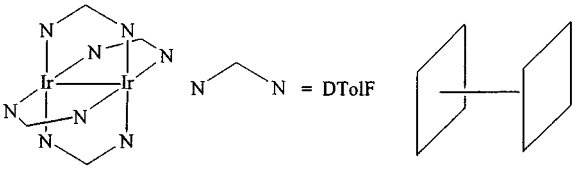

I **II**

Scheme 1

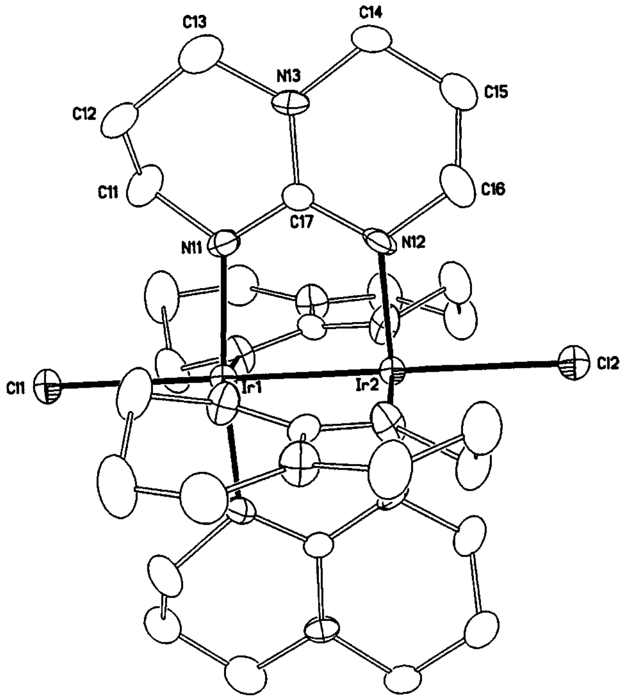

Fig. 1 The molecular structure of $Ir_2(hpp)_4Cl_2$; atoms are drawn at the 50% probability level. Selected bond distances (Å): Ir(1)–Ir(2) 2.495(1), Ir–Cl (av) 2.643[6], Ir–N (av) 2.01[1] Å; N–Ir–Ir–N torsion angle = 11.2(4)°.

Notes and references

† A flask was charged with $IrCl_3$ (0.2 g, 0.66 mmol), Hhpp (0.46 g, 3.3 mmol) and a stirring bar. Ethanol (40 ml) was added and the mixture was refluxed overnight resulting in a brown solution with a small amount of dark solid. All solvent was removed under vacuum and the brown residue dissolved in 10 ml CH_2Cl_2. A purple band was eluted on a silica gel column using a 10 : 1 CH_2Cl_2–MeOH eluent. After the solvent was evaporated, a purple solid, namely $Ir_2(hpp)_4Cl_2$, was isolated in 10% yield (0.034 g, 0.034 mmol). Purple crystals of **1** were grown by the slow diffusion of hexanes into a dichloromethane solution of **1**. IR (KBr, cm^{-1}): 2930w, 2848m, 1700w, 1653w, 1601vw, 1560w, 1526vs, 1465.3s, 1440vs, 1386m, 1309s, 1276m, 1212vs, 1140w, 1071vw, 1031vw, 759m, 407vw. UV–VIS (CH_2Cl_2) [λ/nm(ε/dm^3 mol^{-1} cm^{-1})]: 365 (3900), 396 (3900), 515 (4500), 550 (5700), 701 (6100). ^{1}H NMR ($CDCl_3$): δ 1.81 (br qnt, CH_2), 3.06 (t, CH_2), 5.40 (br, CH_2). $\chi_g = 3.9 \times 10^{-3}$ cm^3 mol^{-1}; $\mu_{obs} = 3.05$ μ_B. Elemental analysis: found (calc.): C, 33.23 (33.40); H, 4.79 (4.80); N, 15.91 (16.67)%.

‡ *Crystal data* for $Ir_2(hpp)_4Cl_2$: $C_{28}H_{48}N_{12}Ir_2Cl_2$, $M = 1008.08$, tetragonal, space group $P4/n$, $a = 9.966(3)$, $c = 15.907(6)$ Å, $V = 1579.8(9)$ Å^3, $Z = 2$, μ(Mo-Kα) = 8.627 mm^{-1}. Data were collected at 213(2) K. The structure, refined on F^2, converged for 1036 unique reflections and 103 parameters to give $R1(F) = 0.038$ and $wR2(F^2) = 0.080$ with a goodness-of-fit of 1.150. CCDC 182/1318. See http://www.rsc.org/suppdata/cc/1999/1427/ for crystallographic data in .cif format.

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