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Air Oxidation of $Ir_2(Cl)_2(COD)_2$ Revisited. The Structures of $[Ir(\mu^2\text{-}Cl)(COD)]_2$ (Ruby Form) and its Oxidation Product, $Ir_2Cl_2(COD)_2(\mu^2\text{-}OH)_2(\mu^2\text{-}O)$

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Abstract

The reaction of $[Ir(COD)(\mu^2\text{-}Cl)]_2$ (ruby form) (**1**) with air in CH_2Cl_2 solution affords in moderate yield a dinuclear complex of Ir(III), $Ir_2(COD)_2Cl_2(\mu^2\text{-}OH)_2(\mu^2\text{-}O)\cdot CH_2Cl_2$ (**2**). The compound **1** crystallizes in the orthorhombic space group *Pbca* with $a = 13.631(4)$, $b = 16.297(5)$, $c = 15.163(4)$ Å, $V = 3368(3)$ Å^3, $Z = 8$. It is a binuclear complex of Ir(I) with square-planar metal coordination. The two squares share the edge defined by the chlorine atoms. The angle between those planes is 86°. The Cl bridges are symmetrical with a mean Ir–Cl bond length of 2.401[4] Å. The Ir··Ir distance is 2.910(1) Å. Compound **2** crystallizes in the orthorhombic space group *Cmcm* with cell dimensions $a = 17.022(4)$, $b = 12.382(5)$, $c = 10.201(4)$ Å, $V = 2150(2)$ Å^3, $Z = 4$. The binuclear molecular complex has a face-sharing bioctahedral configuration with two hydroxyl and one oxo bridging groups. The Ir··Ir distance is 2.868(1) Å.

Introduction

The +II oxidation state of the group 8 transition elements Rh and Ir (d^7 electron configuration) is a relatively unstable one [1]. Among the best defined species are dinuclear complexes containing a metal–metal bond. While there is now a large number of structurally characterized dirhodium compounds containing the $[Rh]^{4+}$ core available [2], examples of $[Ir]^{4+}$ containing compounds are still relatively rare. For example, the bridged tetracarboxylates, $[M_2(O_2CR)_4]$, which are so common for dirhodium have yet to be prepared for iridium.

A possible synthetic route to dinuclear clusters of Ir(II) consists of $2e^-$ oxidative additions to Ir(I) dinuclear species and concomitant formation of a M–M bond. We have recently reported such an example, *viz.*, addition of I_2 to $Ir_2(OMe)_2(COD)_2$ which afforded the M–M bonded compound $Ir_2I_2(\mu^2\text{-}I)_2(COD)_2$. From the latter a trinuclear cluster compound, $Ir_3(COD)_3(\mu^3\text{-}O)_2(\mu^2\text{-}I)$ was obtained upon treatment with $Ag(O_2CCH_3)$ [3].

During our search for potential starting materials for the synthesis of Ir clusters our interest was aroused by a report of a complex whose chemical formulation, Ir(COD)Cl(OH), was suggestive for a divalent oxidation state of the metal [4].

We report here the structure of a dinuclear complex of Ir(III), $Ir_2(COD)_2Cl_2(\mu^2\text{-}OH)_2(\mu^2\text{-}O)$ (**2**), which we obtained by following the procedure in reference [4] to the best of our ability. We also structurally characterized the starting material, the ruby form of $Ir_2(COD)_2Cl_2$ (**1**).

Experimental

Preparation of $Ir_2(COD)_2Cl_2$ (1)

In a standard preparation 800 mg of $IrCl_3\cdot 3H_2O$ and 1.2 ml of 1,5-cyclooctadiene (COD) in a mixture of 4 ml of isopropanol and 5.5 ml of H_2O were heated to 65–70 °C in an atmosphere of argon for 40 h. The red crystalline material thereby obtained was filtered off, washed with cold methanol and dried in air. Yield 75%.

Preparation of $Ir_2(COD)_2Cl_2(\mu^2\text{-}OH)_2(\mu^2\text{-}O)$ (2)

Following ref. 4 this compound is obtained in low yield (10–15%) upon air exposure of a concentrated solution of **1**. It is deposited as pale yellow crystals (brown according to [4]) while the color of the solution gradually changes from red to dark brown. The yield can be increased appreciably when O_2 is bubbled into a dilute solution of **1** in CH_2Cl_2. As above, pale yellow crystals are deposited which lose crystallinity when exposed to air due to loss of solvent.

X-ray Procedures

The crystallographic work for both compounds was routine and followed the general procedures

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TABLE I. Crystal Data for **1** and **2**

	1	**2**
Formula	$Ir_2Cl_2C_{16}H_{24}$	$Ir_2Cl_4O_3C_{17}H_{28}$
Formula weight	671.7	806.62
Space group	*Pbca*	*Cmcm*
Systematic absences	$0kl$: $k = 2n + 1$, $h0l$: $l = 2n + 1$, $hk0$: $h = 2n + 1$	hkl: $h + k = 2n + 1$, $h0l$: $l = 2n + 1$
a (Å)	13.631(4)	17.022(4)
b (Å)	16.297(5)	12.382(5)
c (Å)	15.163(4)	10.201(4)
V (Å^3)	3368(3)	2150(3)
Z	8	4
d_c (g/ cm^3)	2.65	2.49
Crystal size (mm^3)	0.5 × 0.2 × 0.2	0.4 × 0.3 × 0.2
μ(Mo Kα) (cm^{-1})	160.4	128.4
Data collection instrument	Enraf-Nonius CAD-4	Syntex P3
Radiation (monochromated in incident beam)	Mo Kα ($\lambda\bar{\alpha}$ = 0.71073 Å)	
Orientation reflections, number, range (2θ)	25, 22–35	23, 15–30
Temperature (°C)	22 ± 2	22 ± 2
Scan method	ω–2θ	ω–2θ
Data collection range, 2θ, deg	4–45	4–45
Number unique data, total with	2482	875
$F_o^2 > 3\sigma(F_o^2)$	1994	729
Number of parameters refined	181	69
Transmission factors, max./min. (exp.)	1.0/0.23	1.0/0.52
R^a	0.044	0.039
R_w^b	0.062	0.049
Quality-of-fit indicator^c	1.73	1.25
Largest shift/e.s.d., final cycle	0.01	0.03
Largest peak (e/Å^3)	1.4, 1.2 (near Ir)	1.6 (near Ir)

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

described elsewhere [5].* Crystals of **2** were mounted in mother liquor inside Lindemann glass capillaries in order to prevent crystal deterioration due to solvent loss. While the space group *Pbca* in **1** was uniquely determined by the systematic absences, the centrosymmetric choice (*Cmcm*) in **2** was confirmed by successful refinement. Many data pertaining to data collection and refinement are summarized in Table I. Tables II and III contain the fractional coordinates for compounds **1** and **2**, respectively.

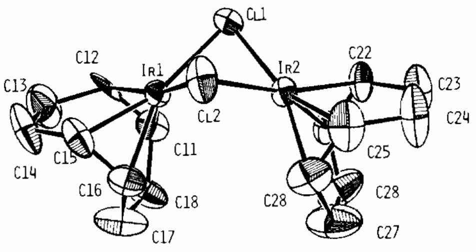

Fig. 1. ORTEP view of [Ir(COD)Cl]$_2$ (**1**). All atoms are represented by their ellipsoids of thermal vibration at the 40% probability level.

Results and Discussion

The Structure of Ir$_2$(COD)$_2$Cl$_2$ (1)

A perspective drawing of the molecular unit is shown in Fig. 1. The dinuclear unit is composed of two iridium atoms which have a square planar arrangement of ligands. The two squares share an edge defined by the bridging Cl atoms. The dihedral angle between the planes is 86°. Although there are no crystallographically imposed symmetry elements the virtual symmetry of the core atoms corresponds to C_{2v}. The Ir··Ir separation is 2.910(1) Å and the average Ir–Cl bond length 2.401[4] Å. Other important bond lengths and angles are given in Table IV.

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*Computing was done by a PDP-11/60 with programs from the package SDP/P with SDP/V simulation.

TABLE II. Table of Positional Parameters and their Estimated Standard Deviations for $Ir_2Cl_2(COD)_2$[a]

Atom	x	y	z	B (Å^2)
Ir1	0.26343(4)	0.11802(4)	0.22562(4)	2.85(1)
Ir2	0.38153(5)	0.24524(4)	0.14272(4)	2.79(1)
Cl1	0.2054(3)	0.2345(3)	0.1441(3)	3.9(1)
Cl2	0.3673(4)	0.2165(3)	0.2972(3)	4.7(1)
C(11)	0.219(1)	0.039(1)	0.125(1)	3.7(4)
C(12)	0.148(1)	0.0404(9)	0.191(1)	4.2(4)
C(13)	0.132(1)	−0.031(1)	0.255(2)	7.3(7)
C(14)	0.201(2)	−0.034(1)	0.329(2)	6.9(6)
C(15)	0.285(1)	0.026(1)	0.321(1)	4.6(4)
C(16)	0.361(1)	0.023(1)	0.254(1)	4.2(4)
C(17)	0.358(1)	−0.050(1)	0.190(2)	6.6(6)
C(18)	0.296(2)	−0.031(1)	0.111(2)	6.0(6)
C(21)	0.394(1)	0.218(1)	0.007(1)	3.7(4)
C(22)	0.389(1)	0.304(1)	0.020(1)	3.7(4)
C(23)	0.470(2)	0.361(1)	0.009(2)	6.5(6)
C(24)	0.546(2)	0.358(2)	0.081(2)	8.3(7)
C(25)	0.519(1)	0.297(2)	0.155(1)	5.7(5)
C(26)	0.526(1)	0.208(2)	0.141(1)	5.7(5)
C(27)	0.558(2)	0.166(2)	0.050(2)	8.4(7)
C(28)	0.480(2)	0.174(2)	−0.019(1)	6.9(7)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

TABLE III. Table of Positional Parameters and their Estimated Standard Deviations for $Ir_2Cl_2(COD)_2(\mu\text{-}OH)_2(\mu\text{-}O)\cdot CH_2Cl_2$ (2)*[a]

Atom	x	y	z	B (Å^2)
Ir	0.41577(3)	0.38141(3)	0.250	2.27(1)
Cl1	0.3666(2)	0.5637(3)	0.250	3.96(9)
O1	0.500	0.4388(7)	0.117(1)	2.8(2)
O2	0.500	0.266(1)	0.250	2.9(3)
Cl2	0.000	0.3967(5)	0.1095(8)	8.7(2)
C1	0.3207(7)	0.3577(8)	0.110(1)	3.8(2)
C2	0.3685(6)	0.2655(8)	0.389(1)	3.6(2)
C3	0.2402(7)	0.3639(9)	0.172(2)	6.3(4)
C4	0.3490(9)	0.1578(9)	0.322(1)	5.8(3)
C5	0.000	0.318(2)	0.250	8(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Synthesis and Structure of $Ir_2(COD)_2Cl_2(\mu^2\text{-}OH)_2(\mu^2\text{-}O)$ (2)

When we followed, to the best of our knowledge, the procedure of reference [4] we isolated compound 2 which crystallizes in the same space group which was originally reported [4]. A computer generated drawing is given in Fig. 2. The molecular complex is best described in terms of a face-sharing bioctahedron. It resides at a site of crystallographic *mm* symmetry. Important bond lengths and angles are given in Table V.

During the structure determination it became apparent, in light of the IR spectrum, that some of the bridges had to be hydroxyl groups. Attempts to locate unequivocally the hydrogen atoms, however, did not meet with success. Careful evaluation of the metric properties together with the IR results and

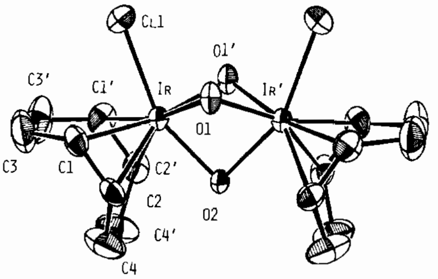

Fig. 2. ORTEP view of $Ir_2Cl_2(COD)_2(\mu\text{-}OH)_2(\mu\text{-}O)$ (2).

TABLE IV. Bond Distances and Angles for $Ir_2(\mu\text{-}Cl)_2(COD)_2$ (1)^a

Bond distances (Å)					
Ir1–Ir2	2.910(1)	Ir2–C(22)	2.10(2)	C(17)–C(18)	1.48(3)
Ir1–Cl1	2.399(5)	Ir2–C(25)	2.06(2)	C(21)–C(22)	1.42(3)
Ir1–Cl2	2.400(5)	Ir2–C(26)	2.06(2)	C(21)–C(28)	1.42(3)
Ir1–C(11)	2.09(2)	C(11)–C(12)	1.40(3)	C(22)–C(23)	1.45(3)
Ir1–C(12)	2.08(2)	C(11)–C(18)	1.57(3)	C(23)–C(24)	1.50(4)
Ir1–C(15)	2.11(2)	C(12)–C(13)	1.53(3)	C(24)–C(25)	1.56(3)
Ir1–C(16)	2.08(2)	C(13)–C(14)	1.46(4)	C(25)–C(26)	1.46(4)
Ir2–Cl1	2.408(4)	C(14)–C(15)	1.50(3)	C(26)–C(27)	1.60(3)
Ir2–Cl2	2.397(4)	C(15)–C(16)	1.44(3)	C(27)–C(28)	1.51(3)
Ir2–C(21)	2.11(2)	C(16)–C(17)	1.54(3)		
Bond angles (°)					
Cl1–Ir1–Cl2	84.2(2)	Cl1–Ir2–C(25)	159.3(7)	C(14)–C(15)–C(16)	126.0(2)
Cl1–Ir1–C(11)	90.7(5)	Cl1–Ir2–C(26)	158.7(8)	C(15)–C(16)–C(17)	117.0(2)
Cl1–Ir1–C(12)	95.9(5)	Cl2–Ir2–C(21)	156.6(6)	C(16)–C(17)–C(18)	112.0(2)
Cl1–Ir1–C(15)	164.6(5)	Cl2–Ir2–C(22)	164.0(5)	C(11)–C(18)–C(17)	115.0(2)
Cl1–Ir1–C(16)	154.9(5)	Cl2–Ir2–C(25)	93.5(6)	C(22)–C(21)–C(28)	125.0(2)
Cl2–Ir1–C(11)	155.9(5)	Cl2–Ir2–C(26)	91.7(6)	C(22)–C(23)–C(24)	115.0(2)
Cl2–Ir1–C(12)	164.6(6)	Ir1–Cl1–Ir2	74.5(1)	C(23)–C(24)–C(25)	113.0(2)
Cl2–Ir1–C(15)	95.0(5)	Ir1–Cl2–Ir2	74.7(1)	C(24)–C(25)–C(26)	121.0(2)
Cl2–Ir1–C(16)	91.6(5)	C(12)–C(11)–C(18)	124.0(2)	C(25)–C(26)–C(27)	124.0(2)
Cl1–Ir2–Cl2	84.1(2)	C(11)–C(12)–C(13)	124.0(2)	C(26)–C(27)–C(28)	112.0(2)
Cl1–Ir2–C(21)	94.3(5)	C(12)–C(13)–C(14)	114.0(2)	C(21)–C(28)–C(27)	116.0(2)
Cl1–Ir2–C(22)	95.2(5)	C(13)–C(14)–C(15)	114.0(2)		

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

TABLE V. Bond Distances and Angles in $Ir_2(Cl)_2(COD)_2(\mu\text{-}OH)_2(\mu\text{-}O)$ (2)^a

Bond distances (Å)					
Ir–Ir′	2.868(1)	Ir–C1	2.179(10)	C1–C3	1.51(2)
Ir–Cl1	2.408(3)	Ir–C2	2.174(9)	C2–C4	1.538(14)
Ir–O1	2.098(7)	Cl2–C5	1.74(2)	C3–C3′	1.58(4)
Ir–O2	2.024(8)	C1–C2	1.402(13)	C4–C4′	1.46(3)
Bond angles (°)					
Cl1–Ir–O1	85.4(2)	O1–Ir–C2	154.1(3)	Ir–O1–Ir′	86.2(4)
Cl1–Ir–O2	155.3(2)	O1–Ir–C2′	93.1(4)	Ir–O2–Ir′	90.2(5)
Cl1–Ir–C1	82.4(3)	O2–Ir–C1	115.5(3)	C2–C1–C3	124.0(1)
Cl1–Ir–C2	119.4(3)	O2–Ir–C2	78.2(3)	C1–C2–C4	126.0(1)
O1–Ir–O1′	80.6(4)	C1–Ir–C1′	82.0(7)	C1–C3–C3	114.9(8)
O1–Ir–O2	75.8(3)	C1–Ir–C2	93.7(4)	C2–C4–C4	116.6(6)
O1–Ir–C1	97.4(4)	C1–Ir–C2	93.7(4)	Cl2–C5–Cl2	111.0(2)
O1–Ir–C1′	167.8(3)	C2–Ir–C2′	81.6(6)		

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

the observed diamagnetism, on the other hand, leads plausibly to an assignment of the oxidation states of the metal centers.

For the molecule to be diamagnetic an even electron count is required for the dinuclear unit thus restricting the possible combinations of oxidation states to II/II, III/III and IV/IV. The latter can be discarded since it entails three oxo-bridges which is in contradiction to the strong OH signal in the IR spectrum. Of the remaining combinations the II/II (d^7–d^7) one requires electron pairing, *viz.*, a formal M–M single bond in order to concur with the observed diamagnetism. We observe, however, a geometrical arrangement which is indicative of a repulsive rather than an attractive interaction between the metal centers despite the apparently

TABLE VI. Analytical Data

	Ir	Cl	C	H
Experimental value[a]	47.37	16.04	25.94	3.48
Calc. for $Ir(COD)Cl(OH)\cdot 0.5CH_2Cl_2$[a]	48.62	17.93	25.82	3.57
Calc. for $Ir_2(COD)_2Cl_2(\mu^2\text{-}OH)_2(\mu^2\text{-}O)\cdot CH_2Cl_2$	47.66	17.58	25.29	3.47

[a] From ref. 4.

short M–M distance of 2.868(1) Å. The geometrical properties of face-sharing bioctahedra have been treated in detail before [6]. The values for the idealized M–O_{br}–M and O_{br}–M–O_{br} angles are 70.53° and 90°, respectively. In **2** we find the bond angles around the metal centers to be acute (average 79[1]°) and the bridging angles much larger (average 85[2]°) than the theoretical value of 70.53°. The iridium atoms thus experience a repulsive interaction which is always present but which can be overcome by attractive forces in the case of M–M bonding. Another argument against the di-positive oxidation state is that it entails a 20-electron count at each metal center which is unlikely in light of the stability of the compound.

We therefore propose **2** to be a dinuclear complex of Ir(III). The observed octahedral coordination and the diamagnetic behaviour due to a t_{2g}^6 electron configuration are in agreement with previous data [1]. The bridges must then consist of two hydroxy and one oxo group. It is tempting to assign the hydroxo functions to the two symmetry related atoms O1 and O1′ and the oxo bridge to O2. Our observed bond distances corroborate this assignment in that the Ir–O1 distance is significantly longer than the Ir–O2 bond length ($\Delta/\sigma = 9$). Finally, we find that the crystallographically established composition is in at least as good agreement with the reported chemical analysis as the initially proposed structures (Table VI.

Acknowledgement

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Supplementary Material

Tables of anisotropic displacement parameters are available from author F.A.C.

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