



Crystal structure of di- μ -chlorido-bis[dichlorido-bis(methanol- κ O)iridium(III)] dihydrate: a surprisingly simple chloridoiridium(III) dinuclear complex with methanol ligands

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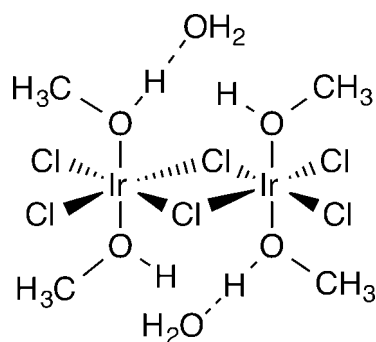
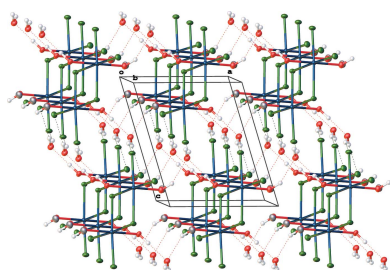
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The reaction between $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ in methanol led to the formation of small amounts of the title compound, $[\text{Ir}_2\text{Cl}_6(\text{CH}_3\text{OH})_4] \cdot 2\text{H}_2\text{O}$, which consists of two IrCl_4O_2 octahedra sharing an edge *via* chloride bridges. The molecule lies across an inversion center. Each octahedron can be envisioned as being comprised of four chloride ligands in the equatorial plane with methanol ligands in the axial positions. A lattice water molecule is strongly hydrogen-bonded to the coordinating methanol ligands and weak interactions with coordinating chloride ligands lead to the formation of a three-dimensional network. This is a surprising structure given that, while many reactions of iridium chloride hydrate are carried out in alcoholic solvents, especially methanol and ethanol, this is the first structure of a chloridoiridium compound with only methanol ligands.

1. Chemical context

The use of alcoholic solvents with $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ for the formation of cyclopentadienyl or olefin iridium complexes is exceedingly common (Herde *et al.*, 2007; Liu *et al.*, 2008, 2011; Morris *et al.*, 2014). Lately, we have been investigating the syntheses of half-sandwich iridium complexes with varying tetramethylalkylcyclopentadienyl ligands (Morris *et al.*, 2014). In all cases, the reaction takes place between $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ and the tetramethylalkylcyclopentadiene in methanol, either under thermal or microwave conditions. In most cases, the yields of Cp^{*R} iridium chlorido-bridged dimers are good to excellent. Several reactions to synthesize Cp^{*R} iridium complexes with R = long-chain alkyls such as *n*-hexyl, *n*-heptyl and *n*-octyl produced good yields of the desired $[\text{Cp}^{*R}\text{IrCl}_2]_2$ compounds but, in one instance, only produced a few crystals which turned out to be those of the title compound. Given the number of reactions that are carried out with $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ in methanol, that this is the first time this compound has been seen by us or by any others active in the field is surprising.



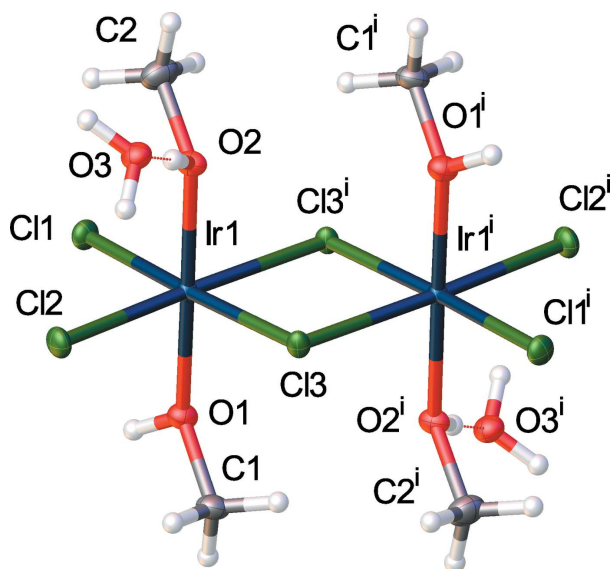


Figure 1
The full molecular unit of the title compound with hydrogen-bonded lattice water molecules [symmetry code (i) $-x + 1, -y + 1, -z + 2$]. Displacement ellipsoids are drawn at the 50% probability level.

2. Structural commentary

The title structure (Fig. 1) consists of two iridium-centered octahedra sharing one edge *via* chloride bridges. For each octahedron, there are two terminal chloride ligands in the same plane as the bridging chloride ligands. The axial positions that complete the octahedra are occupied by O-bonded methanol ligands. One of the methanol ligands on each iridium atom is hydrogen-bonded to a lattice water. The two iridium-centered octahedra are related by an inversion center. The Ir–Cl bridges are symmetrical with identical Ir–Cl bond lengths of 2.385 (1) Å with two of the Ir–Cl bonds equivalent by symmetry and the unique bonds coincidentally equivalent [2.3847 (10) and 2.3846 (11) Å]. The only structure similar to the title compound currently in the Cambridge Structural

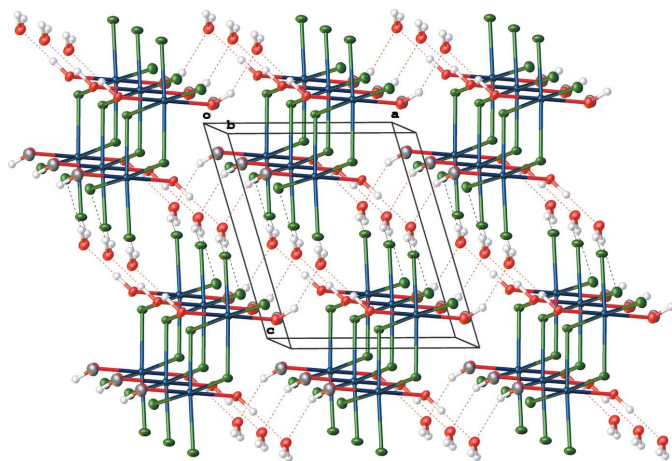


Figure 2
Packing diagram of the title compound showing the hydrogen-bonding (dashed lines) network. Displacement ellipsoids are drawn at the 50% probability level.

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1-H1\cdots O3^i$	0.86 (1)	1.96 (3)	2.752 (5)	151 (4)
$O2-H2\cdots O3$	0.87 (1)	1.78 (1)	2.647 (5)	179 (2)
$O3-H3A\cdots Cl2^{ii}$	0.85	2.39	3.208 (4)	160
$O3-H3B\cdots Cl1^{iii}$	0.85	2.45	3.285 (3)	166

Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y + 2, -z + 1$.

Database (CSD version 5.35 with updates, Groom & Allen, 2014) is CCDC: CLESIR, bis(μ -chlorido)tetrachloridotetrakis(diethylsulfide)diiridium(III) (Williams *et al.*, 1980). The structural similarities between CLESIR and the title compound are that both contain octahedrally coordinated iridium atoms with the octahedra sharing one edge *via* Ir–Cl–Ir bridges. There are also two terminal chloride ligands on each iridium for both compounds. In the case of CLESIR, however, the remaining ligands on the iridium are diethylsulfido ligands. An additional difference is that, for the title compound, all chloride ligands are in the equatorial plane with methanol ligands occupying axial positions. For CLESIR, the diethylsulfido ligands on one iridium atom occupy axial positions but occupy equatorial positions on the second iridium.

3. Supramolecular features

Each lattice water molecule forms four hydrogen bonds linking four different iridium-centered dimers. Table 1 lists the various parameters describing the hydrogen bonding. As a donor, the water participates in two O–H \cdots Cl bonds to chloride ligands on different molecules while, as acceptor, the water participates in two O–H \cdots O bonds to methanol oxygen atoms on two additional molecules. A search of the CSD for O–H \cdots Cl bonds between lattice water and chloride attached to any transition metal followed by analysis in *Mercury* (Macrae *et al.*, 2008) show that the O \cdots Cl distances have a mean of 3.151 Å with a mean deviation of 0.055 Å. The two O \cdots Cl distances of 3.208 (4) and 3.285 (3) Å for this structure places the distances at the high end of the range. However, when acting as acceptors, the lattice water displays O(methanol)–O(water) distances of 2.752 (5) and 2.647 (5) Å. A search of the CSD with analysis by *Mercury* (Macrae *et al.*, 2008) uncovers a mean O(donor) \cdots O(acceptor) distance of 2.742 Å with a mean deviation of 0.085 Å, putting the donor–acceptor distances at the mean and slightly below the mean of these types of hydrogen bonds. Fig. 2 shows the hydrogen-bonding network that is created throughout the lattice of the title compound with the methanol methyl groups removed for clarity.

4. Database survey

A survey of the CSD found only 11 structures of iridium with methanol ligands (methoxide ligands were excluded from the search but they added only an additional eight structures to

the result). Analysis with *Mercury* (Macrae *et al.*, 2008) found that Ir—O bonds in this small subset ranged from 2.185 to 2.317 Å with a mean of 2.251 Å and a standard deviation of 0.042 Å. The Ir—O bond lengths of the title compound of 2.066 (3) and 2.057 (3) Å are significantly smaller than the low end of this range. The small number of samples and the variety of structures available for comparison do not permit any clear conclusions as to the significance of these distances. All of the structures are of iridium(III) but the title compound is the only one with chloride as the sole other ligand set on each metal. While this structure determination was carried out at 100 K compared with room temperature for most of the other compounds with methanol ligands, such a significant bond shortening would not be expected based solely on temperature (Macchi & Sironi, 2004).

5. Synthesis and crystallization

IrCl₃·xH₂O and 1-heptyl, 2,3,4,5-tetramethylcyclopentadiene were mixed in a round-bottom flask with 15 mL of MeOH and the reaction mixture was refluxed for two days. This procedure has been successfully used to synthesize a number of pentaalkyliridium chloride compounds in the past. After cooling to room temperature, the round-bottom flask was placed into a freezer overnight. There was no evidence of any product crystallization. The reaction mixture was then evaporated to dryness, yielding a tarry mixture. The tarry mixture was dissolved in diethyl ether and allowed to evaporate slowly. After the ether had evaporated, the mixture was again very tarry in appearance, but this time with a few crystals obvious in the flask. The structure of the title compound was determined from one of those crystals. It is unclear why this reaction did not proceed normally.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms bonded to C atoms were included in calculated positions with C—H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. H atoms bonded to water O atoms were included in calculated positions with O—H = 0.85 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. The H atoms bonded to methanol O atoms were refined independently with isotropic displacement parameters.

Acknowledgements

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Table 2
Experimental details.

Crystal data	
Chemical formula	[Ir ₂ Cl ₆ (CH ₄ O) ₄] ₂ ·2H ₂ O
<i>M_r</i>	380.68
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.1445 (4), 7.4876 (5), 8.6362 (7)
α , β , γ (°)	73.597 (6), 75.596 (5), 89.404 (5)
<i>V</i> (Å ³)	428.37 (5)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	16.46
Crystal size (mm)	0.14 × 0.11 × 0.09
Data collection	
Diffractometer	Agilent Xcalibur Eos Gemini ultra
Absorption correction	Gaussian (<i>CrysAlis PRO</i> ; Agilent, 2014)
<i>T</i> _{min} , <i>T</i> _{max}	0.184, 0.342
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	7987, 2817, 2575
<i>R</i> _{int}	0.040
(sin θ/λ) _{max} (Å ⁻¹)	0.750
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.028, 0.055, 1.03
No. of reflections	2817
No. of parameters	93
No. of restraints	6
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	1.67, -1.94

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

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Crystal structure of di- μ -chlorido-bis[dichloridobis(methanol- κ O)iridium(III)] dihydrate: a surprisingly simple chloridoiridium(III) dinuclear complex with methanol ligands

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Di- μ -chlorido-bis[dichloridobis(methanol- κ O)iridium(III)] dihydrate

Crystal data

$[\text{Ir}_2\text{Cl}_6(\text{CH}_3\text{O})_4]\cdot 2\text{H}_2\text{O}$

$M_r = 380.68$

Triclinic, $P\bar{1}$

$a = 7.1445$ (4) Å

$b = 7.4876$ (5) Å

$c = 8.6362$ (7) Å

$\alpha = 73.597$ (6)°

$\beta = 75.596$ (5)°

$\gamma = 89.404$ (5)°

$V = 428.37$ (5) Å³

$Z = 2$

$F(000) = 348$

$D_x = 2.951$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3445 reflections

$\theta = 4.0\text{--}32.1^\circ$

$\mu = 16.46$ mm⁻¹

$T = 100$ K

Prism, clear light orange

$0.14 \times 0.11 \times 0.09$ mm

Data collection

Agilent Xcalibur Eos Gemini ultra diffractometer

Radiation source: Enhance (Mo) X-ray Source, Agilent

Graphite monochromator

Detector resolution: 16.0122 pixels mm⁻¹

ω scans

Absorption correction: gaussian (CrysAlis PRO; Agilent, 2014)

$T_{\min} = 0.184$, $T_{\max} = 0.342$

7987 measured reflections

2817 independent reflections

2575 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\max} = 32.2^\circ$, $\theta_{\min} = 4.0^\circ$

$h = -10 \rightarrow 10$

$k = -11 \rightarrow 11$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.055$

$S = 1.03$

2817 reflections

93 parameters

6 restraints

Primary atom site location: structure-invariant direct methods

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0194P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.67 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.94 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ir1	0.64307 (2)	0.65568 (2)	0.81418 (2)	0.01042 (5)
Cl1	0.82335 (16)	0.93834 (15)	0.74853 (14)	0.0167 (2)
Cl2	0.72146 (16)	0.65918 (17)	0.53518 (13)	0.0177 (2)
Cl3	0.45411 (15)	0.36814 (14)	0.89543 (12)	0.01298 (19)
O1	0.9022 (5)	0.5412 (5)	0.8390 (4)	0.0169 (7)
H1	1.0118 (19)	0.603 (3)	0.785 (5)	0.025*
O2	0.3880 (4)	0.7770 (5)	0.7908 (4)	0.0151 (6)
H2	0.328 (5)	0.759 (4)	0.720 (4)	0.023*
C1	0.9356 (7)	0.3485 (7)	0.8412 (6)	0.0208 (10)
H1A	0.9287	0.3317	0.7366	0.031*
H1B	0.8388	0.2669	0.9302	0.031*
H1C	1.0615	0.3197	0.8584	0.031*
C2	0.3605 (8)	0.9702 (7)	0.7877 (7)	0.0274 (12)
H2A	0.4497	1.0503	0.6912	0.041*
H2B	0.3835	0.9897	0.8868	0.041*
H2C	0.2303	0.9984	0.7831	0.041*
O3	0.2082 (5)	0.7157 (5)	0.5754 (4)	0.0182 (7)
H3A	0.2516	0.6327	0.5284	0.027*
H3B	0.2060	0.8178	0.5013	0.027*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ir1	0.01073 (8)	0.01068 (8)	0.00999 (8)	-0.00075 (6)	-0.00180 (6)	-0.00389 (6)
Cl1	0.0172 (5)	0.0126 (5)	0.0189 (5)	-0.0039 (4)	-0.0030 (4)	-0.0034 (4)
Cl2	0.0209 (5)	0.0215 (6)	0.0104 (5)	0.0007 (4)	-0.0018 (4)	-0.0058 (4)
Cl3	0.0167 (5)	0.0117 (5)	0.0113 (4)	-0.0021 (4)	-0.0022 (4)	-0.0056 (4)
O1	0.0149 (15)	0.0173 (17)	0.0199 (16)	0.0019 (13)	-0.0048 (13)	-0.0074 (13)
O2	0.0152 (15)	0.0185 (17)	0.0161 (15)	0.0035 (13)	-0.0073 (12)	-0.0092 (13)
C1	0.018 (2)	0.020 (2)	0.025 (2)	0.0057 (19)	-0.0036 (19)	-0.009 (2)
C2	0.028 (3)	0.017 (2)	0.036 (3)	0.003 (2)	-0.009 (2)	-0.006 (2)
O3	0.0196 (17)	0.0180 (17)	0.0184 (16)	0.0041 (14)	-0.0076 (13)	-0.0051 (14)

Geometric parameters (Å, °)

Ir1—C11	2.3400 (11)	O2—C2	1.452 (6)
Ir1—C12	2.3267 (11)	C1—H1A	0.9600
Ir1—C13 ⁱ	2.3847 (10)	C1—H1B	0.9600
Ir1—C13	2.3846 (11)	C1—H1C	0.9600
Ir1—O1	2.066 (3)	C2—H2A	0.9600
Ir1—O2	2.057 (3)	C2—H2B	0.9600
C13—Ir1 ⁱ	2.3847 (10)	C2—H2C	0.9600
O1—H1	0.864 (10)	O3—H3A	0.8500
O1—C1	1.456 (6)	O3—H3B	0.8498
O2—H2	0.867 (9)		
C11—Ir1—C13 ⁱ	92.90 (4)	C1—O1—H1	105.1 (16)
C11—Ir1—C13	177.08 (4)	Ir1—O2—H2	121.2 (16)
C12—Ir1—C11	91.47 (4)	C2—O2—Ir1	121.9 (3)
C12—Ir1—C13 ⁱ	175.59 (4)	C2—O2—H2	104.7 (15)
C12—Ir1—C13	91.44 (4)	O1—C1—H1A	109.5
C13—Ir1—C13 ⁱ	84.19 (4)	O1—C1—H1B	109.5
O1—Ir1—C11	83.45 (10)	O1—C1—H1C	109.5
O1—Ir1—C12	90.01 (9)	H1A—C1—H1B	109.5
O1—Ir1—C13 ⁱ	91.08 (9)	H1A—C1—H1C	109.5
O1—Ir1—C13	96.79 (10)	H1B—C1—H1C	109.5
O2—Ir1—C11	94.91 (10)	O2—C2—H2A	109.5
O2—Ir1—C12	90.73 (9)	O2—C2—H2B	109.5
O2—Ir1—C13	84.81 (10)	O2—C2—H2C	109.5
O2—Ir1—C13 ⁱ	88.30 (9)	H2A—C2—H2B	109.5
O2—Ir1—O1	178.22 (13)	H2A—C2—H2C	109.5
Ir1—C13—Ir1 ⁱ	95.81 (4)	H2B—C2—H2C	109.5
Ir1—O1—H1	121.2 (16)	H3A—O3—H3B	109.5
C1—O1—Ir1	121.8 (3)		

Symmetry code: (i) $-x+1, -y+1, -z+2$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1 \cdots O3 ⁱⁱ	0.86 (1)	1.96 (3)	2.752 (5)	151 (4)
O2—H2 \cdots O3	0.87 (1)	1.78 (1)	2.647 (5)	179 (2)
O3—H3A \cdots C12 ⁱⁱⁱ	0.85	2.39	3.208 (4)	160
O3—H3B \cdots C11 ^{iv}	0.85	2.45	3.285 (3)	166

Symmetry codes: (ii) $x+1, y, z$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, -y+2, -z+1$.