Kgaugelo C. Tapala and Hadley S. Clayton*

The crystal structure of bis(μ_2 -iodido)-bis(η^6 -benzene)-bis(iodido)-diosmium(II), $C_{12}H_{12}I_4Os_2$

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Abstract

$C_{12}H_{12}I_4Os_2$, orthorhombic, *Pbca* (no. 61), $a = 11.9720(5)$ Å, $b = 10.4991(4)$ Å, $c = 13.2810(6)$ Å, $V = 1669.36(12)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0349$, $wR_{ref}(F^2) = 0.0848$, $T = 173(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All reagents are commercially available and were used without further purification. Potassium osmate $K_2[OsO_2(OH)_4]$ (1.020 g, 2.77 mmol) was refluxed in hydroiodic acid/ethanol (50 mL 3:2 v/v) at 150 °C for 8 h to generate the $[OsI_6]^{2-}$ intermediate. To the cooled reaction mixture was added

Table 1: Data collection and handling.

Crystal:	Red plate
Size:	$0.45 \times 0.23 \times 0.04$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	22.6 mm^{-1}
Diffractometer, scan mode:	Bruker D8 Venture Photon, ω
θ_{max} , completeness:	28.0° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	26,320, 2011, 0.062
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1934
$N(\text{param})_{\text{refined}}$:	70
Programs:	Bruker [1], SHELX [2], WinGX [3], PLATON [4]

1,3-cyclohexadiene (3 mL, 31 mmol). The reaction mixture was then heated under microwave irradiation (140 °C, 400 W) for 20 min. A red crystalline product was obtained upon cooling, which was collected by filtration and washed with hexane (10 mL). Yield 67% (0.974 g, 0.933 mmol). Crystals were obtained as red plates directly upon cooling the reaction solution to room temperature.

Experimental details

Intensity data was determined on a Bruker Venture D8 Photon CMOS diffractometer with graphite-monochromated Mo $K\alpha_1$ ($\lambda = 0.71073$ Å) radiation at 173 K using an Oxford Cryostream 600 cooler. Data reduction was carried out using the program SAINT-Plus, version 6.02 [1] and empirical absorption corrections were made using SADABS [1]. The structure was solved in the WinGX [2] Suite of programs,

*Corresponding author: **Hadley S. Clayton**, Chemistry Department, Unisa Science Campus, University of South Africa, Johannesburg, South Africa, E-mail: clayths@unisa.ac.za. <https://orcid.org/0000-0001-5472-853X>

Kgaugelo C. Tapala, Chemistry Department, Unisa Science Campus, University of South Africa, Johannesburg, South Africa. <https://orcid.org/0000-0002-8530-9191>

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	U_{iso}^*/U_{eq}
C1	0.6057 (5)	0.8142 (6)	0.6068 (5)	0.0304 (18)
H1	0.665895	0.800638	0.652153	0.036*
C2	0.5024 (6)	0.8536 (6)	0.6431 (4)	0.0307 (17)
H2	0.492051	0.866963	0.71328	0.037*
C3	0.4143 (5)	0.8735 (6)	0.5768 (6)	0.0337 (18)
H3	0.343693	0.900424	0.601663	0.04*
C4	0.4294 (5)	0.8540 (6)	0.4742 (5)	0.0293 (17)
H4	0.369178	0.86756	0.428918	0.035*
C5	0.5327 (6)	0.8146 (6)	0.4379 (4)	0.0284 (18)
H5	0.54302	0.801235	0.36779	0.034*
C6	0.6208 (4)	0.7947 (6)	0.5042 (5)	0.0274 (17)
H6	0.691379	0.767774	0.479406	0.033*
I1	0.33304 (5)	0.58731 (6)	0.69308 (4)	0.01803 (15)
I2	0.38608 (4)	0.52380 (5)	0.41369 (4)	0.01314 (14)
Os1	0.47884 (3)	0.68286 (3)	0.55414 (2)	0.00830 (11)

using intrinsic phasing through SHELXT [3] and refined using SHELXL-2018-3 [3]. All C bound hydrogen atoms were placed at idealized positions and refined as riding atoms with isotropic parameters 1.2 times those of their parent atoms. SIMU and DELU commands were used to constraint the anisotropic displacement parameters for all the C atoms and AFIX66 to idealize the phenyl ring. Diagrams and publication material were generated using ORTEP-3 [2], and PLATON [4].

Comment

Metal-arenes are a well established subclass of organo-metallic compounds since the synthesis of the archetypal complex $[Cr(\eta^6-C_6H_6)_2]$ by Fischer and Hafner in 1955 [5]. Dinuclear metal-arene compounds of the heavier transition metals such as ruthenium and osmium are extensively employed in organometallic chemistry as precursors [6, 7], providing synthetic pathways for various organometallic compounds with applications in catalysis [8] and bio-organometallic chemistry [9, 10].

The title compound crystallizes in the space group *Pbca*, with a centrosymmetric molecular unit. The dinuclear complex adopts a pseudo-octahedral geometry at each Os^{2+} ion, with the hexahaptic benzene ring occupying three coordination sites together with two bridging iodido ligands and one terminal iodido ligand occupying a further three coordination sites.

For the terminal iodido ligand the Os–I bond length is measured as 2.7310(6) $\text{\AA}$ while for the two bridging iodido ligands Os–I bond lengths of 2.7388(6) and 2.7396(6) $\text{\AA}$ are measured. The distance from the benzene ring centroid to

the Os center is calculated to be 1.664 $\text{\AA}$. The benzene ligand is symmetrically coordinated to the metal with the six Os–C bond lengths in the narrow range of 2.165–2.171 $\text{\AA}$ with no evidence of ring puckering. The distance between the two Os^{2+} ions is 4.131 $\text{\AA}$ which confirms the absence of a direct metal-metal bond.

The crystal growth of the title compound is supported by C–H $\cdots$ I interactions. There are also strong intermolecular π – π -interactions observed between benzene rings to adjacent complexes with a plane-to-plane distance of 3.324 $\text{\AA}$.

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