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Crystal structure of dibromido μ -oxalato- $\kappa^2 O, O': \kappa^2 O'', O'''$ - η^6 -*p*-cymenediosmium(II), $C_{22}H_{28}Br_2O_4Os_2$

Table 1: Data collection and handling.

Crystal:	Yellow blocks
Wavelength:	Size $0.63 \times 0.52 \times 0.25$ mm
μ :	Mo $K\alpha$ radiation ($0.71073 \text{ \AA}$)
Diffractometer, scan mode:	138.7 cm^{-1}
$2\theta_{\text{max}}$, completeness:	Broker APEX-II, φ and ω
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	56° , $>99\%$
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	34419, 2911, 0.090
$N(\text{param})_{\text{refined}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2701
Programs:	139
	Broker programs [2], SHELX [3],
	WinGX [4], Platon [5]

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Abstract

$C_{22}H_{28}Br_2O_4Os_2$, orthorhombic, *Pbca* (no. 61), $a = 10.8433(5) \text{ \AA}$, $b = 11.8395(5) \text{ \AA}$, $c = 18.7871(8) \text{ \AA}$, $V = 2411.87(18) \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.0511$, $wR_{\text{ref}}(F^2) = 0.1061$, $T = 173 \text{ K}$.

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The title structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The synthesis was modified from a procedure reported by Yan and co-workers [1]. To a solution of $[Os(\eta^6\text{-}p\text{-cymene})Br_2]$ (2.348 g, 2.33 mmol) in CH_2Cl_2 – CH_3OH (1:1, 40 mL) was added an excess of $(NH_4)_2C_2O_4 \cdot H_2O$ (4.180 g, 29.53 mmol). The mixture was stirred at room temperature overnight and

then filtered to remove NH_4Br and unreacted $(NH_4)_2C_2O_4 \cdot H_2O$. The filtrate was concentrated to about 2 mL under reduced pressure to give a yellow oil. The oil was redissolved in CH_2Cl_2 and diethyl ether was added to precipitate the product. The formed precipitate was separated by filtration, washed with ether, and dried *in vacuo*, to give a yellow powder. Yield 1.785 g (82%).

Experimental details

The collection method involved ω -scans of width 0.5° . Data reduction was carried out using SAINT-Plus version 6.02.6 software, and SADABS was used to proceed empirical absorption corrections [2]. The crystal structure was solved through direct methods using SHELXS-97 [3]. Hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms with $d(C-H) = 0.95 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$. Diagrams and publication material were generated using WinGX,[4] and PLATON [5].

Discussion

In recent years, arene-ruthenium complexes have attracted considerable interest as potential anticancer agents and alternatives to platinum based metallopharmaceuticals such as Cisplatin. In contrast, relatively little research has been carried out on the arene-osmium analogues and limited structural data are available for complexes of this type. In this paper we report the crystal structure of the binuclear osmium complex, $[Os_2(\mu_2\text{-}C_2O_4)Br_2(\eta^6\text{-}p\text{-cymene})]$.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C1	1.0759(10)	0.3443(8)	−0.0069(9)	0.048(4)
H1	1.143	0.3411	0.0239	0.058*
C2	1.0940(11)	0.3365(9)	−0.0816(10)	0.059(4)
H2	1.1735	0.3248	−0.0987	0.071*
C3	0.9961(12)	0.3460(9)	−0.1311(7)	0.045(3)
C4	0.8755(11)	0.3625(8)	−0.1017(5)	0.036(2)
H4	0.8087	0.3702	−0.1323	0.044*
C5	0.8555(10)	0.3673(7)	−0.0283(6)	0.031(2)
H5	0.7756	0.3777	−0.0114	0.037*
C6	0.9526(11)	0.3570(7)	0.0209(6)	0.033(2)
C7	0.9269(18)	0.3517(12)	0.0994(7)	0.075(5)
H7A	0.9967	0.3197	0.1235	0.112*
H7B	0.8555	0.3055	0.1077	0.112*
H7C	0.912	0.4265	0.1172	0.112*
C8	1.009(2)	0.3335(15)	−0.2117(10)	0.108(9)
H8	0.9434	0.2783	−0.2212	0.129*
C9	1.1187(19)	0.267(2)	−0.2318(13)	0.119(9)
H9A	1.1286	0.2681	−0.2825	0.179*
H9B	1.1082	0.19	−0.2162	0.179*
H9C	1.1905	0.2983	−0.2096	0.179*
C10	0.963(2)	0.428(2)	−0.2500(10)	0.124(9)
H10A	1.0219	0.4883	−0.2484	0.186*
H10B	0.8867	0.4531	−0.2287	0.186*
H10C	0.9479	0.407	−0.2986	0.186*
C11	0.9473(8)	0.0076(7)	0.0263(5)	0.0233(18)
O1	0.8988(6)	0.1037(5)	0.0301(4)	0.0265(14)
O2	1.0841(6)	0.0778(5)	−0.0615(4)	0.0267(14)
Br1	0.82357(10)	0.09135(10)	−0.12990(7)	0.0413(3)
Os1	0.95702(3)	0.21503(3)	−0.05285(2)	0.02387(12)

The oxalate-bridged, binuclear osmium complex (*cf.* the figure) is remarkably stable and can be utilized as a synthon for potential metallopharmaceuticals [6]. In addition to the potential of the complex as an anticancer agent, the non-innocent bridging oxalate ligand is of interest because of its potential for facilitating electronic interactions between redox centres due to its planarity and electron delocalization [7].

In this structure, both osmium(II) centres are in a pseudooctahedral environment composed of a facially coordinated cymene ligand, an O,O'-chelating oxalato ligand and a bromido ligand. The *p*-cymene rings are planar with Os—C distances in the range 2.137(11)–2.179(10) Å. The distance from the cymene ring centroid to the Os centre is calculated to be 1.636 Å. The osmium-cymene moieties are linked through a planar, rigid oxalate bridging ligand which adopts a bis-bidentate coordination mode. The oxalate bridge exerts a small but significant structural *trans* influence on the C—C bond length within the *p*-cymene ring, with the shortest C—C bond within the ring at 1.397(15) Å positioned *trans* to the oxalate group.

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References

1. Yan H; Süß-Fink G; Neels A; Stoeckli-Evans H: Mono-, di- and tetra-nuclear *p*-cymene ruthenium complexes containing oxalato ligands. *J. Chem. Soc., Dalton Trans.* **22** (1997) 4345–4350.
2. Bruker: SAINT-Plus and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, (2004).
3. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr.* **A64** (2008) 112–122.
4. Farrugia, L. J.: WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Cryst.* **32** (1999) 837–838.
5. Spek, A. L.: Structure validation in chemical crystallography. *Acta Crystallogr.* **D65** (2009) 148–155.
6. Peacock, A. F. A; Melchart, M.; Deeth, R.J; Habtemariam, A; Parsons, S; Sadler, P. J: Osmium(II) and ruthenium(II) arene maltolato complexes: rapid hydrolysis and nucleobase binding. *Chem. Eur. J.* **13** (2007) 2601–2613.
7. Tarlton, M. L; Anderson, A. E; Weberski, M. P; Riart-Ferrer, X; Nelson, B. M; McLauchlan, C. C: Synthesis, characterization and electrochemical properties of μ -oxalate bridged vanadium(III) and (IV) dimers incorporating the Kläui ligand, CpP^{OR}Co (R = Me, Et). *Inorg. Chim. Acta* **420** (2014) 159–165.