

Structure of a Bis(osmate ester) Produced by Addition of Osmium Tetroxide to Diethyl 3,4-Furandicarboxylate

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Abstract. [μ -2,3-Bis(ethoxycarbonyl)tetrahydro-2,3,4,5-furantetrolato- $O^2, O^3: O^4, O^5$]-bis(dioxodipyridyl-osmium), $[\text{Os}_2(\text{O})_4(\text{C}_{10}\text{H}_{12}\text{O}_9)(\text{C}_5\text{H}_5\text{N})_4]$, $M_r = 1037.06$, monoclinic, $C2/c$, $a = 18.593$ (3), $b = 13.240$ (3), $c = 16.639$ (3) Å, $\beta = 122.10$ (1)°, $V = 3469.8$ (11) Å³, $Z = 4$, $D_m = 1.961$, $D_x = 1.99$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 73.9$ cm⁻¹, $F(000) = 1984$, $T = 298$ K, $R = 0.0384$ for the 4235 data which were considered observed ($F_o \geq 3\sigma F_o$) of the 5029 unique data collected. Addition of two OsO_4 /(pyridine)₂ moieties to diethyl 3,4-furandicarboxylate yielded a bis(osmate ester), with Os atoms located *trans* to each other relative to the tetrahydrofuran ring. The tetrahydrofuran ring has the expected half-chair pucker.

Introduction. The addition of OsO_4 /pyridine to unsaturated substrates followed by hydrolysis of the resulting oxoosmium(VI) ester is a useful route for preparation of *cis* diols (Sheldon & Kochi, 1981; Mijs & de Jonge, 1986; Shröder, 1980). The osmate esters of pyrimidine (Beer, Stern, Carmalt & Mohlenrich, 1966; Marzilli, 1977) or ribose moieties (Conn, Kim, Sudath, Blattmann & Rich, 1974) in nucleic acids and unsaturated components in proteins (Deetz & Behrman, 1980) and lipids provide heavy-atom-containing derivatives for X-ray and electron-microscopic analysis. Chemical modification of cytosine and adenine bases in nucleic acids to yield the corresponding etheno derivatives provides additional sites for OsO_4 addition (Marzilli, Hanson, Kapili, Rose & Beer, 1978). Recently, OsO_4 /pyridine treatment of native DNA has been shown to exhibit high specificity for single-strand regions, and thereby served as a reliable means of identifying sites of single base-pair mismatches in abnormal genes (Cotton, Rodrigues & Campbell, 1988).

We have previously studied the reaction of furan and substituted furans (Hartman & Rose, 1981) as well as furyl-modified polynucleotides (Rose & Beer, 1979) with OsO_4 /pyridine and OsO_4 /bipyridine. We

now report the X-ray structure of the bis(osmate ester) formed by addition of OsO_4 to diethyl 3,4-furandicarboxylate.

Experimental. *Preparation of dipyridyl osmate ester.* Crystals began to form after approximately 24 h from a solution of aqueous OsO_4 , pyridine and diethyl 3,4-furandicarboxylate and were collected, washed briefly with water, and air dried. The crystal selected for analysis, with dimensions $0.15 \times 0.17 \times 0.18$ mm, was cleaved from a larger crystal containing inclusions and was mounted on a glass fiber. Density was measured by flotation in $\text{CH}_2\text{I}_2/\text{CCl}_4$ and 1,2-dibromoethane/toluene.

Structure determination. A Siemens R3m/V diffractometer was used for data collection. Cell parameters were refined by least squares on 40 reflections in the 2θ range 4.0 – 25.0° . Intensities were collected with $\text{Mo } K\alpha$ radiation in the range $3.5 \leq 2\theta \leq 60.0^\circ$ using the ω -scan technique. The data were corrected for Lorentz and polarization effects as well as secondary extinction as described by Zachariasen (1967); extinction correction 0.00018. An absorption correction was applied using ψ -scan modeling of the crystal as a pseudo-ellipsoid, min., max. transmission coefficients 0.154, 0.375. Data with $F_o \geq 3\sigma(F_o)$ were considered observed (4235 of 5029 unique data). Patterson synthesis (Siemens *SHELXTL-Plus*) yielded Os positions and difference maps revealed the remaining non-H atoms. Full-matrix least squares on F was used to refine the structure. H atoms were added in idealized positions and refined as atoms riding on their bonding partners. The final conventional $R = 0.0384$ and $wR = 0.0505$ where $w = 1.000/[\sigma^2(F) + 0.0001012(F^2)]$. The largest peak and hole in the final difference map were 1.07 and -0.78 e Å⁻³, respectively. hkl ranged from 0 to 24, 0 to 19, and -24 to 24, respectively. The final $(\Delta/\sigma)_{\text{max}}$ was 0.002. Three standard reflections (202 , 111 and 002) were collected every 47 reflections and no discernible degradation was indicated (variation in standard intensities < 1%). The entire structure determination, using tabulated atomic scattering factors, as well as the production of the plots

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Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$)

	x	y	z	U_{eq}^*
Os	3536 (1)	2925 (1)	3021 (1)	40 (1)
O(1)	4634 (2)	3618 (3)	3619 (3)	50 (2)
O(2)	3994 (2)	2087 (3)	2430 (3)	45 (2)
O(3)	3823 (3)	2111 (3)	3966 (3)	53 (2)
O(4)	2985 (2)	3749 (3)	2075 (3)	49 (2)
N(1A)	2337 (3)	2109 (3)	2342 (3)	43 (2)
C(2A)	1785 (4)	2219 (4)	1415 (4)	50 (2)
C(3A)	1033 (4)	1668 (6)	935 (5)	60 (3)
C(4A)	847 (5)	1001 (5)	1441 (6)	67 (4)
C(5A)	1409 (4)	901 (5)	2384 (5)	59 (3)
C(6A)	2142 (4)	1475 (5)	2822 (5)	54 (3)
N(1B)	3104 (3)	3893 (3)	3729 (3)	46 (2)
C(2B)	2430 (3)	4499 (5)	3260 (5)	52 (3)
C(3B)	2192 (5)	5152 (5)	3727 (6)	65 (4)
C(4B)	2664 (6)	5198 (6)	4704 (7)	80 (5)
C(5B)	3375 (5)	4590 (7)	5186 (6)	78 (4)
C(6B)	3559 (4)	3941 (6)	4678 (5)	65 (3)
O	5000	3892 (4)	2500	61 (3)
C(1)	5135 (4)	3276 (4)	3277 (4)	49 (2)
C(2)	4885 (3)	2200 (3)	2879 (4)	40 (2)
C(1E)	5361 (3)	1413 (4)	3658 (4)	44 (2)
C(2E)	5370 (6)	-292 (6)	4080 (6)	81 (4)
C(3E)	4892 (11)	-1153 (10)	3771 (11)	281 (14)
O(1E)	6005 (3)	1561 (3)	4402 (3)	64 (2)
O(2E)	4971 (3)	517 (3)	3400 (3)	63 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

were performed by the *SHELXTL-Plus* package (Sheldrick, 1987).

Discussion. The final atomic parameters with their e.s.d.'s are listed in Table 1.* Bond lengths and angles for the non-H atoms, with the associated e.s.d.'s, appear in Table 2. A view of the molecule, together with the atom-labeling scheme, is given in Fig. 1. The structure shown clearly indicates the *trans* relationship of the [OsO₄(py)₂] groups relative to the tetrahydrofuran ring. This finding parallels our earlier conclusions for a bis(osmate ester) of a related furan, which was based on the spectroscopic properties of the product (Hartman & Rose, 1981). The tetrahydrofuran ring exhibits the expected half-chair pucker, as seen in the stereoview in Fig. 2. The structure of the osmate ester moiety was very similar to that reported for the OsO₄/bipyridine esters of adenosine (Conn, Kim, Sudath, Blattmann & Rich,

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53368 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (\AA) and angles ($^\circ$)

Os—O(1)	1.960 (4)	Os—O(2)	1.952 (5)
Os—O(3)	1.739 (4)	Os—O(4)	1.734 (4)
Os—N(1A)	2.177 (5)	Os—N(1B)	2.164 (6)
O(1)—C(1)	1.399 (10)	O(2)—C(2)	1.418 (7)
N(1A)—C(2A)	1.331 (7)	N(1A)—C(6A)	1.335 (10)
C(2A)—C(3A)	1.392 (9)	C(3A)—C(4A)	1.384 (13)
C(4A)—C(5A)	1.353 (10)	C(5A)—C(6A)	1.382 (9)
N(1B)—C(2B)	1.335 (7)	N(1B)—C(6B)	1.339 (8)
C(2B)—C(3B)	1.382 (13)	C(3B)—C(4B)	1.379 (12)
C(4B)—C(5B)	1.382 (12)	C(5B)—C(6B)	1.371 (14)
O—C(1)	1.433 (8)	O—C(1A)	1.433 (8)
C(1)—C(2)	1.536 (7)	C(2)—C(1E)	1.526 (7)
C(2)—C(2A)	1.532 (15)	C(1E)—O(1E)	1.195 (6)
C(1E)—O(2E)	1.337 (7)	C(2E)—C(3E)	1.367 (16)
C(2E)—O(2E)	1.443 (9)		
O(1)—Os—O(2)	84.7 (2)	O(1)—Os—O(3)	95.4 (2)
O(2)—Os—O(3)	95.5 (2)	O(1)—Os—O(4)	96.9 (2)
O(2)—Os—O(4)	96.1 (2)	O(3)—Os—O(4)	163.8 (2)
O(1)—Os—N(1A)	177.9 (2)	O(2)—Os—N(1A)	93.3 (2)
O(3)—Os—N(1A)	84.2 (2)	O(4)—Os—N(1A)	83.9 (2)
O(1)—Os—N(1B)	92.0 (2)	O(2)—Os—N(1B)	176.6 (2)
O(3)—Os—N(1B)	84.2 (2)	O(4)—Os—N(1B)	84.8 (2)
N(1A)—Os—N(1B)	90.1 (2)	Os—O(1)—C(1)	112.3 (3)
Os—O(2)—C(2)	112.0 (3)	Os—N(1A)—C(2A)	119.6 (5)
Os—N(1A)—C(6A)	122.0 (3)	C(2A)—N(1A)—C(6A)	118.4 (5)
N(1A)—C(2A)—C(3A)	121.9 (7)	C(2A)—C(3A)—C(4A)	119.0 (6)
C(3A)—C(4A)—C(5A)	118.7 (7)	C(4A)—C(5A)—C(6A)	119.7 (8)
N(1A)—C(6A)—C(5A)	122.4 (6)	Os—N(1B)—C(2B)	122.9 (5)
Os—N(1B)—C(6B)	119.0 (4)	C(2B)—N(1B)—C(6B)	118.0 (6)
N(1B)—C(2B)—C(3B)	122.0 (6)	C(2B)—C(3B)—C(4B)	119.8 (7)
C(3B)—C(4B)—C(5B)	118.1 (10)	C(4B)—C(5B)—C(6B)	118.8 (7)
N(1B)—C(6B)—C(5B)	123.3 (6)	C(1)—O—C(1A)	110.6 (6)
O(1)—C(1)—O	110.4 (4)	O(1)—C(1)—C(2)	111.2 (6)
O—C(1)—C(2)	105.8 (5)	O(2)—C(2)—C(1)	109.0 (5)
O(2)—C(2)—C(1E)	111.3 (5)	C(1)—C(2)—C(1E)	111.2 (4)
O(2)—C(2)—C(2A)	109.1 (5)	C(1)—C(2)—C(2A)	101.6 (5)
C(1E)—C(2)—C(2A)	114.2 (5)	C(2)—C(1E)—O(1E)	125.3 (5)
C(2)—C(1E)—O(2E)	111.3 (4)	O(1E)—C(1E)—O(2E)	123.5 (5)
C(3E)—C(2E)—O(2E)	111.3 (8)	C(1E)—O(2E)—C(2E)	116.2 (4)

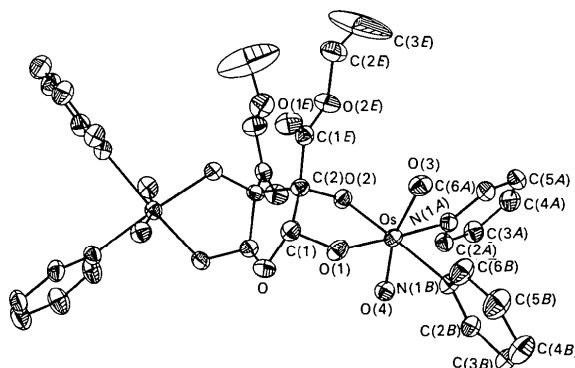


Fig. 1. Perspective view of one of the molecules with the atom-numbering scheme. H atoms are omitted and thermal ellipsoids are depicted at the 30% probability level for clarity.

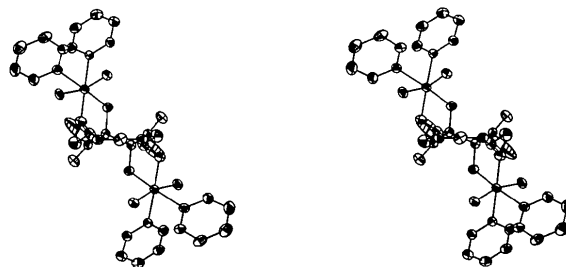


Fig. 2. Stereoview down the b axis, illustrating the conformation of the tetrahydrofuran ring and the *trans* relationship of the osmyl groups.

1974) and thymine (Neidle & Stuart, 1976). The O(1C)—Os(1)—O(1D) angle of the *trans*-oxoosmyl group was found to be 163.8 (2)°, compared to 164 and 162° for the adenosine and thymine esters, respectively.

The mechanism of formation of osmate esters was long thought to proceed *via* oxygen attack on the double bond in a [3 + 2] cycloaddition. Compelling evidence now shows that a four-membered heterocyclic organoosmium intermediate is formed initially, and this rearranges to give the osmate ester (Sharpless, Teranishi & Backväll, 1977; Tomioka, Nakajima, Iitaka & Koga, 1988). In addition to this thermal synthesis, osmate esters can be prepared photochemically by irradiation of charge-transfer bands [OsO₄⁻, Ar⁺] observed upon mixing of OsO₄ with various arene or alkene substrates (Wallis & Kochi, 1987). An X-ray structure determination of the resulting 2:1 adducts of benzene and also of anthracene likewise showed a *trans* orientation of the osmate groups (Wallis & Kochi, 1988).

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Structure of the Protonated Pentamethylcyclopentadienylrhodium Dimethylbutadiene Complex, a Compound with an Agostic $M\cdots H\cdots C$ Interaction

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Abstract. (2,3-Dimethylbutenyl)(pentamethylcyclopentadienyl)rhodium tetrafluoroborate, [Rh(C₁₀H₁₅)(C₆H₁₁)] [BF₄], $M_r = 408.10$, monoclinic, C_c , $a = 8.418$ (3), $b = 14.185$ (3), $c = 14.840$ (3) Å, $\beta = 91.98$ (2)°, $V = 1771$ (1) Å³, $Z = 4$, $D_x = 1.531$ g cm⁻³, $\mu(\text{Mo } K\alpha) = 8.89$ cm⁻¹, $\lambda = 0.71073$ Å, $F(000) = 832$, $R = 0.032$ for 3609 observed reflections. The compound has the typical appearance of a sandwich complex with two parallel π -bonded ligands. An Rh \cdots H \cdots C bond to one of the methyl groups of the butenyl ligand is indicated by the bond parameters Rh \cdots H = 1.88 (3), H—C = 1.12 (2) and Rh \cdots C = 2.351 (5) Å, making this molecule a further typical example of an organometallic

compound with an 'agostic' metal-to-hydrogen bond.

Introduction. The stoichiometric activation of carbon-hydrogen bonds by transition-metal complexes has received considerable attention in recent years. A similar activation is also encountered in many catalytic transformations of hydrocarbons and as such is of vast industrial importance. Complexes with $M\cdots H\cdots C$ interactions are thought to be important intermediates in such conversions. This has to some extent been verified by the observation that complexes with an $M\cdots H\cdots C$ moiety can, under special circumstances, be isolated and spectroscopically as well as structurally characterized. This type of bonding is sometimes referred to as 'agostic'

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