

Preliminary communication

PREPARATION, X-RAY STRUCTURAL ANALYSIS AND SOME
PROPERTIES OF DICHLOROTETRAKIS(*n*-BUTYRATO)DIOSMIUM(III)

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(Received March 5th, 1982)

The paramagnetic compounds $[\text{Os}_2(\text{OCOR})_4\text{Cl}_2]$ ($\text{R} = n\text{-C}_3\text{H}_7, \text{C}_2\text{H}_5, \text{CH}_2\text{Cl}$) have been synthesised by reaction of $[\text{Os}(\text{OCOCH}_3)_2\text{Cl}]_n$ with the appropriate acids and the binuclear tetracarboxylate bridged structure confirmed by X-ray analysis for $\text{R} = n\text{-C}_3\text{H}_7$, (Os-Os distance 2.301 Å; cf. the related $[\text{Os}_2(\text{hp})_4\text{Cl}_2]$ - $(\text{CH}_3\text{CN})_2$; Os-Os , 2.357 Å) ($\text{hp} = 2\text{-hydroxypyridine anion}$).

In the last two decades, extensive studies on binuclear complexes containing multiple metal-to-metal bonds have been published [1]. However, until the recent report of the crystal structure of $[\text{Os}_2(\text{hp})_4\text{Cl}_2]$, ($\text{hp} = 2\text{-hydroxypyridine anion}$) [2], no examples of such complexes containing osmium had been found.

In this preliminary communication, we now wish to report the preparation, X-ray structural analysis and some properties of the closely related $[\text{Os}_2(\text{OCO-}n\text{-C}_3\text{H}_7)_4\text{Cl}_2]$ (I) compound. This was prepared in reasonable yield (50–60%) by reaction at 140°C for 8 h of the sparingly soluble $[\text{Os}(\text{OCOCH}_3)_2\text{Cl}]_n^*$ with an excess of *n*-butyric acid. On cooling the solution slowly, dark green needle-shaped crystals of the product are deposited. Similar reactions with propionic and monochloroacetic acid give the corresponding $[\text{Os}(\text{OCOR})_2\text{Cl}]_n$ ($\text{R} = \text{C}_2\text{H}_5$ (25%), CH_2Cl (50%)). As for the acetate complex [3,4] the latter compounds are not sufficiently soluble for molecular weight determination** but for compound I, osmometric molecular weight measure-

*This complex, prepared in 25% yield in our laboratory [3], by reaction of $\text{Na}_2[\text{OsCl}_6]$ with acetic acid/acetic anhydride has been obtained very recently [4] in higher yield (55%) by addition of a little concentrated hydrochloric acid to this reaction mixture.

**However, in the mass spectra of all these compounds the appearance of the parent ions $[\text{Os}_2(\text{OCOR})_4\text{Cl}_2]^+$, together with fragmentation patterns corresponding to successive loss of two chloride groups strongly support their formulation as binuclear species.

ments in benzene confirmed the retention in solution of the binuclear unit established by X-ray structural analysis.

Crystal data for I: $C_{16}H_{20}Cl_2O_8Os_2$, monoclinic, space group $P2_1/n$ with cell parameters, $a = 6.789(2)$, $b = 11.790(1)$, $c = 14.923(1)$ Å, $\beta = 98.211(18)^\circ$, $U = 1182$ Å³, $Z = 2$, $D_c = 2.25$ g cm⁻³; monochromated Mo- K_α radiation 0.71069 Å, $\mu = 116.8$ cm⁻¹.

Structure determination: A crystal of dimension $0.35 \times 0.18 \times 0.04$ mm was used to collect 2100 unique data out to $\theta = 25^\circ$ on a CAD 4 diffractometer. An empirical absorption correction was applied. The structure was solved by Patterson and difference Fourier methods. All non-hydrogen atoms have been located and refined anisotropically to give $R = 0.044$ from the 1686 reflections with $I > 2.5\sigma(I)$. The weighting scheme was $w = 1.0/(\sigma^2(F) + 0.00089 F^2)$. Fractional coordinates are given in Table 1 and selected bond lengths and angles in Table 2.

The molecule is a dimer lying on a crystallographic inversion centre with each osmium ion exhibiting octahedral coordination (Fig. 1). The Os—Os and Os—Cl distances of 2.301 and 2.417 Å, respectively, are comparable with those found in the related $[Os_2(hp)_4Cl_2]2CH_3CN$ (2.357 and 2.505 Å, respectively) [2]. The butyrate shows both trans ($C(8)-C(7)-C(6)-C(5) = 176^\circ$) and gauche ($C(4)-C(3)-C(2)-C(1) = 54^\circ$) conformations.

Interestingly, variable temperature magnetic measurements from 300–188 K

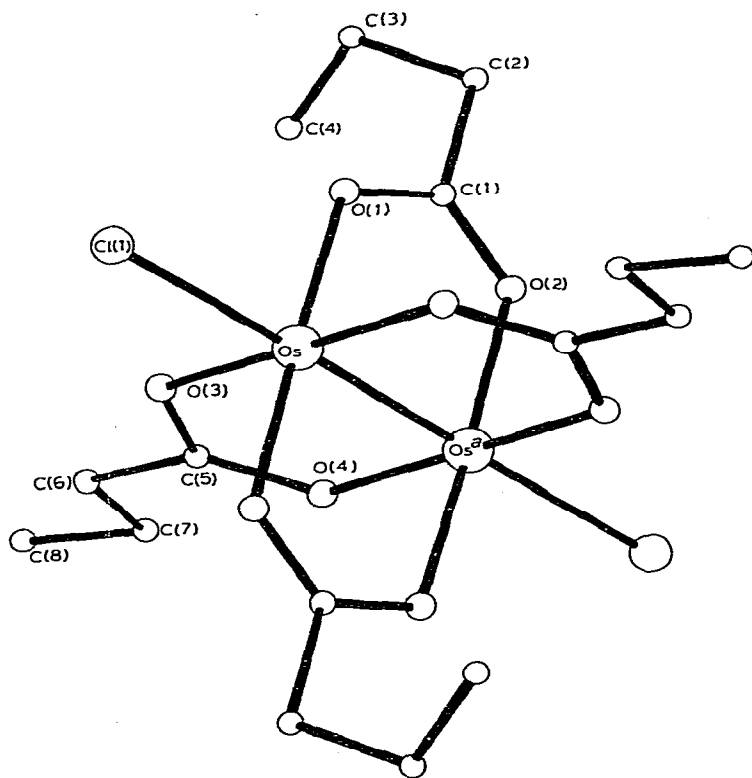


Fig. 1. Molecular structure of $[Os_2(OCO-n-C_3H_7)_4Cl_2]$.

TABLE 1
FRACTIONAL COORDINATES OF ATOMS WITH STANDARD DEVIATIONS

	<i>x</i>	<i>y</i>	<i>z</i>
Os	0.08828(6)	0.44036(4)	0.45944(3)
Cl(1)	0.2845 (6)	0.3171 (3)	0.3776 (3)
O(1)	-0.1208 (12)	0.4622 (7)	0.3504 (6)
O(2)	-0.2921 (12)	0.5767 (6)	0.4292 (6)
C(1)	-0.2664 (18)	0.5238 (10)	0.3565 (8)
C(2)	-0.4205 (20)	0.5423 (13)	0.2736 (10)
C(3)	-0.3295 (28)	0.5942 (19)	0.1989 (12)
C(4)	-0.2152 (30)	0.6979 (16)	0.2219 (15)
O(3)	0.2344 (13)	0.5736 (6)	0.4192 (6)
O(4)	-0.0672 (12)	0.3092 (6)	0.5015 (6)
C(5)	0.1977 (18)	0.6709 (11)	0.4461 (9)
C(6)	0.3123 (20)	0.7659 (11)	0.4113 (12)
C(7)	0.2366 (23)	0.8809 (14)	0.4287 (13)
C(8)	0.3576 (27)	0.9675 (14)	0.3840 (13)

TABLE 2
BOND LENGTHS (Å) AND BOND ANGLES (°)

Bond lengths (Å)	
Os—Os	2.301(1)
Os—Cl(1)	2.417(3)
Os—O(1)	2.018(8)
Os ^a —O(2)	2.015(8)
C(1)—O(1)	1.241(14)
C(1)—O(2)	1.284(15)
C(1)—C(2)	1.518(25)
C(2)—C(3)	1.482(21)
C(3)—C(4)	1.462(26)
Os—O(3)	1.996(7)
Os ^a —O(4)	2.022(8)
C(5)—O(3)	1.252(14)
C(5)—O(4)	1.284(15)
C(5)—C(6)	1.499(18)
C(6)—C(7)	1.486(21)
C(7)—C(8)	1.523(25)
Bond angles (°)	
Cl(1)—Os—Os ^a	177.96(10)
O(1)—Os—Os ^a	89.27(23)
O(2)—Os—Os ^a	88.55(23)
O(3)—Os—Os ^a	89.79(24)
O(4)—Os—Os ^a	88.23(23)
Os—O(1)—C(1)	119.41(8)
O(1)—C(1)—O(2)	123.5(10)
C(1)—O(2)—Os ^a	119.2(7)
Os—O(3)—C(5)	119.6(8)
O(3)—C(5)—O(4)	123.3(11)
C(5)—O(4)—Os ^a	119.04(8)

^a Represents the atom related by $\bar{x}, \bar{y}, \bar{z}$.

on dichloromethane solutions of the butyrate and propionate (by Evans' method [5]) reveal that both compounds are paramagnetic. However, the magnitude of μ_{eff} (e.g. for R = n-C₃H₇, μ_{eff} decreases from 1.15 BM/Os at 300 K to 1.02 BM/Os at 188 K), is indicative of considerable antiferromagnet-

ic interactions between the osmium(III) ions*. Although further studies, both in the solid state and over a wider range of temperatures, are now required to substantiate these data, it seems reasonable to suggest for these $[\text{Os}_2(\text{OCOR})_4\text{Cl}_2]$ complexes that there is an appreciable population of a spin triplet state, (perhaps corresponding to the central electronic configuration $\sigma^2\pi^4\delta^2\pi^{*2}$ or $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*1}$), at higher temperatures with the singlet ground state, (arising from the $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration), becoming increasingly favoured as the temperature is lowered.

Furthermore, cyclic voltammetric and alternating current voltammetric studies on I in $\text{CH}_2\text{Cl}_2/0.25\text{ M n-Bu}_4\text{NBF}_4$ at 20°C show a one-electron, reversible oxidation (+0.53 V)*** but no further redox steps are observed up to the solvent limit, even at 208 K. For $[\text{Os}_2(\text{OCOC}_2\text{H}_5)_4\text{Cl}_2]$, however, in addition to the reversible oxidation step at +0.57 V, irreversible oxidation and reduction waves are found at +1.28 and -1.54 V, respectively.

Although there is no electrochemical evidence for formation of stable formally mixed-valence $[\text{Os}_2(\text{OCOR})_4\text{Cl}_2]^-$ anions, (cf. the X-ray analysis of $\text{Cs}[\text{Ru}_2(\text{OCOME})_4\text{Cl}_2]$ [8]), the recent brief report [4] of the synthesis of $[\text{Os}_2(\text{OCOMe})_4\text{Cl}(\text{C}_5\text{H}_5\text{N})]$ and $[\text{Os}_2(\text{OCOMe})_4(\text{C}_5\text{H}_5\text{N})_2]\text{Cl}$ from $[\text{Os}_2(\text{OCOMe})_2\text{Cl}]_n$ illustrates that a range of such $\text{Os}_2^{\text{II,III}}$ (or Os_2^{5+}) complexes can be readily isolated. Therefore, comparative studies of their magnetic and optical properties with those of the unusual $[\text{Os}_2^{\text{III,IV}}(\text{OCOR})_4\text{Cl}_2]^+$ cations are now planned.

Finally, preliminary studies show that, like the related binuclear transition metal carboxylates $[\text{M}_2(\text{OCOR})_4]$ ($\text{M} = \text{Mo}, \text{Rh}$ etc.) [1], the carboxylate bridges in $[\text{Os}_2(\text{OCOR})_4\text{Cl}_2]$ are readily replaced by a variety of potential bidentate ligands. For example, reaction of I with $\text{Na}[\text{S}_2\text{CNMe}_2]$ gives $[\text{Os}(\text{S}_2\text{CNMe}_2)_2\text{Cl}]_n$ and further studies on the physicochemical properties of such compounds are now in progress.

Acknowledgements. We thank the SERC for financial support (DAT), Dr. D.K. Vattis and Ms. J.H. Leslie for assistance with the magneto- and electro-chemical measurements respectively, Mr. M.J. Deighton for experimental assistance and Johnson-Matthey PLC for loans of sodium hexachlorosmate (IV).

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*Under the same conditions *mer*- $[\text{OsCl}_3(\text{PMe}_2\text{Ph})_3]$ shows the behaviour expected for a magnetically dilute osmium(III) complex [6] i.e. $\mu_{\text{eff}} = 1.70\text{ BM}$ (almost temperature invariant).

**In support of this proposal, recent SCF-X α -SW calculations on $[\text{Ru}_2(\text{O}_2\text{CH})_4]^+$ etc. and related species indicate an electronic configuration $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*1}$ with a very small energy separation between the π^* and δ^* orbitals [7].

***All $E_{1/2}$ values are measured with respect to a Ag/AgI reference electrode at which ferrocene is oxidised at +0.60 V.