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Structural and Mass Spectral Studies on Some Multiply Bonded Diosmium Tetracarboxylate Compounds

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The compounds $Os_2(O_2CCH_3)_4Cl_2$, *1, and* $Os_2(O_2CC_2H_5)_4Cl_2$, *2, have been structurally characterized. Both compounds crystallize in space group* $P2_1/n$. *For 1 the unit cell parameters are* $a = 6.546(1)$ Å, $b = 8.950(1)$ Å, $c = 12.533(1)$ Å, $\beta = 90.17(1)°$ *and* $Z = 2$; *for 2 they are* $a = 6.792(2)$ Å, $b = 10.519(3)$ Å, $c = 13.372(4)$ Å, $\beta = 89.27(3)°$ *and* $Z = 2$. *Both molecules have approximate* D_{4h} *symmetry with important dimensions as follows: for 1, Os≡Os 2.314(1)* Å, *Os–Cl 2.448(2)* Å; *for 2, Os≡Os 2.316(2)* Å, *Os–Cl 2.430(5)* Å. *The mass spectra of these compounds as well as that of* $Os_2(O_2CC_3H_7)_4Cl_2$, *3, are reported and discussed.*

Introduction

The first report of a compound containing an Os≡Os triple bond, appeared in 1980 [1], and described the synthesis and X-ray crystal structures of $Os_2(hp)_4Cl_2 \cdot S$ ($S = Et_2O$ or $2CH_3CN$; hp = anion of 2-hydroxypyridine). Shortly thereafter two independent reports of the synthesis of the tetracarboxylate complex, $Os_2(O_2CMe)_4Cl_2$, *1*, appeared [2, 3]. One of these reports [2] went on to describe the reactions of the acetate with a variety of ligands; the other [3] dealt particularly with the conversion of the acetate to $Os_2(O_2CR)_4Cl_2$ compounds with $R = C_2H_5$ and C_3H_7, *2* and *3*, respectively, and the characterization of these derivatives as dimers by a variety of techniques. An X-ray crystallographic analysis [3, 4] of the butyrate has unequivocally shown that this compound has the structure characteristic of dinuclear transition metal carboxylates [5].

Since the studies just cited are the only ones so far published on multiply bonded diosmium compounds and because these compounds possess unusual magnetic properties it was clear that further information on these complexes is required. Towards this end we report here the results of crystal structure determinations of compounds *1* and *2*. As reported previously [3, 4], the mass spectra of compounds of this type all show strong parent ion peaks corresponding to the binuclear cations, $[Os_2(O_2CR)_4Cl_2]^+$, and fragmentation patterns due to successive loss of chloride ions. A more detailed examination reveals that a variety of organic fragments are also lost in a manner consistent with the important valence states of each osmium in the binuclear unit being +2.5, +3.0 and +3.5.

Experimental

Preparations

All three compounds were prepared as previously described [4].

Mass Spectral Studies

These were carried out on an A.E.I. MS-902 spectrometer operating at 70 eV. Spectra were calibrated by addition of perfluoroalkanes.

X-ray Crystallographic Procedures

The structures of *1* and *2* were obtained by using the same general procedures as described elsewhere [6, 7]. Crystal data and information pertaining to the collection of data and refinement of the structures is summarized in Table I for both compounds.

Results and Discussion

Crystal and Molecular Structures

Compounds *1* and *2* form crystals that are quasi-isomorphous. Tables II and III list the atomic positional parameters and the isotropic equivalent thermal vibration parameters. In each case the dinuclear molecule resides on a crystallographic center of inversion. Tables IV and V list the bond lengths

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TABLE I. Crystallographic Parameters.

Formula	$Os_2Cl_2O_8C_8H_{12}$	$Os_2Cl_2O_8C_{12}H_{20}$
Formula weight	687.49	743.59
Space group	$P2_1/n$	$P2_1/n$
Systematic absences	h0l, h + l = 2n; 0k0, k = 2n	h0l, h + l = 2n; 0k0, k = 2n
a, Å	6.546(1)	6.792(2)
b, Å	8.950(1)	10.512(3)
c, Å	12.533(1)	13.372(4)
α, degrees		
β, degrees	90.17(1)°	89.27(3)°
γ, degrees		
V, $Å^3$	733.5(4)	955.4(8)
Z	2	2
d_{calc}, g/cm^3	3.112	2.585
Crystal size, mm	0.1 × 0.1 × 0.1	0.4 × 0.1 × 0.05
μ(Mo Kα), cm^{-1}	177.3	132.6
Data collection instrument	CAD-4	Syntex P$\bar{1}$
Radiation (monochromated in incident beam)	Mo	Mo
Orientation reflections, number, range (2θ)	25, 5 –21	15, 24–29
Temperature, °C	25	25
Scan method	$2\theta - \omega$	$2\theta - \omega$
Data col. range, 2θ, deg.		5–50°
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	2214, 1540	778, 775
Number of parameters refined	91	105
Trans. factors, max., min.	99.62%, 70.03%	99.85%, 95.67%
R^a	0.037	0.028
$R_w{}^b$	0.045	0.042
Quality-of-fit indicator^c	1.13	1.23
Largest shift/esd, final cycle	0.35	0.83
Largest peak, e/$Å^3$	1.2	1.1

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bR_w = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1\sigma^2(|F_o|)$. ^{c}Quality of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

TABLE II. Positional Parameters and Their Estimated Standard Deviations for $Os_2(O_2CCH_3)_4Cl_2$, *1*.

Atom	x	y	z	B(A2)
Os(1)	−0.11246(5)	−0.07713(4)	−0.04523(3)	1.391(5)
Cl(1)	−0.3623(4)	−0.2299(3)	−0.1413(2)	2.65(5)
O(1)	0.271(1)	0.1019(8)	−0.0905(6)	2.1(1)
O(2)	0.054(1)	−0.2555(9)	−0.0023(6)	2.1(1)
O(3)	−0.270(1)	0.1079(8)	−0.0863(6)	1.9(1)
O(4)	−0.061(1)	0.0547(9)	0.1767(6)	2.1(1)
C(1)	0.220(1)	−0.234(1)	0.0580(7)	1.9(2)
C(2)	−0.218(2)	−0.032(1)	0.1752(8)	2.0(2)
C(3)	0.338(2)	−0.369(1)	0.0880(9)	2.8(2)
C(4)	0.338(2)	0.052(2)	−0.2753(8)	2.8(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3) × [*a*2 × B(1, 1) + *b*2 × B(2, 2) + *c*2 × B(3, 3) + *ab*(cos gamma) × B(1, 2) + *ac*(cos beta) × B(1, 3) + *bc*(cos alpha) × B(2, 3)].

TABLE III. Positional Parameters and Their Estimated Standard Deviations for $Os_2(O_2CC_2H_5)_4Cl_2$, *2*.

Atom	x	y	z	B(A2)
Os(1)	0.1055(1)	0.07705(7)	0.03027(5)	2.36(1)
Cl(1)	0.3444(7)	0.2300(5)	0.0903(4)	4.1(1)
O(3)	0.265(1)	0.060(1)	−0.0984(8)	2.9(2)
O(4)	−0.258(1)	0.065(1)	−0.0930(8)	3.0(2)
C(6)	−0.321(3)	−0.096(2)	0.316(1)	5.1(5)
C(4)	−0.202(3)	0.025(2)	0.166(1)	2.9(4)
C(5)	0.329(3)	−0.031(2)	−0.260(1)	4.3(5)
O(1)	−0.058(2)	0.091(1)	0.1566(8)	3.2(3)
O(2)	−0.060(2)	0.210(1)	−0.0359(8)	3.3(3)
C(1)	−0.218(2)	0.180(2)	−0.088(1)	2.5(3)*
C(2)	−0.337(2)	0.273(2)	−0.137(1)	3.3(4)
C(3)	−0.307(3)	0.412(2)	−0.099(2)	4.7(5)

*Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3) × [*a*2 × B(1, 1) + *b*2 × B(2, 2) + *c*2 × B(3, 3) + *ab*(cos gamma) × B(1, 2) + *ac*(cos beta) × B(1, 3) + *bc*(cos alpha) × B(2, 3)].

and angles in the acetate and propionate, respectively. The Os–Os and Os–Cl distances in these two compounds lie within the range previously established for formally triply bonded diosmium compounds, *viz.*, 2.301(1) Å and 2.417(3) Å in $Os_2(O_2CC_3H_7)_4Cl_2$ [4] to 2.357(1) Å and 2.500(5) Å in $Os_2(hp)_4Cl_2 \cdot 2CH_3CN$ [1]. Although the Os–Os distances found in these compounds differ significantly in a statistical

TABLE IV. Bond Distances and Angles in $Os_2(O_2CCH_3)_4Cl_2$, *1*.

Bond distances, Å			
Os(1)–Os(1)	2.314(1)	O(1)–C(2)	1.281(12)
Os(1)–Cl(1)	2.448(2)	O(4)–C(2)	1.286(12)
Os(1)–O(1)	2.004(7)	O(2)–C(1)	1.337(11)
Os(1)–O(2)	2.006(7)	O(3)–C(1)	1.229(13)
Os(1)–O(3)	2.017(6)	C(1)–C(3)	1.480(13)
Os(1)–O(4)	2.009(7)	C(2)–C(4)	1.492(13)
Bond angles, Deg.			
Os(1)–Os(1)–Cl(1)	177.16(7)	O(1)–C(2)–O(4)	121.6(9)
Os(1)–Os(1)–O(1)	88.9(2)	O(2)–C(1)–O(3)	120.6(8)
Os(1)–Os(1)–O(2)	89.9(2)	O(2)–C(1)–C(3)	117.0(10)
Os(1)–Os(1)–O(3)	87.7(2)	O(3)–C(1)–C(3)	122.5(9)
Os(1)–Os(1)–O(4)	89.0(2)	O(1)–C(2)–C(4)	119.5(9)
Os(1)–O(1)–C(2)	120.5(6)	O(4)–C(2)–C(4)	119.0(10)
Os(1)–O(2)–C(1)	118.7(6)		
Os(1)–O(3)–C(1)	123.1(6)		
Os(1)–O(4)–C(2)	119.9(7)		

TABLE V. Bond Distances and Angles in $Os_2(O_2CC_2H_5)_4Cl_2$, *2*.

Bond distances, Å			
Os(1)–Os(1)	2.316(1)	O(2)–C(1)	1.32(2)
Os(1)–Cl(1)	2.430(5)	O(4)–C(1)	1.25(2)
Os(1)–O(1)	2.014(10)	C(1)–C(2)	1.43(2)
Os(1)–O(2)	2.008(11)	C(2)–C(3)	1.57(3)
Os(1)–O(3)	2.028(10)	C(4)–C(5)	1.53(2)
Os(1)–O(4)	2.006(11)	C(5)–C(6)	1.53(3)
O(1)–C(4)	1.21(2)		
O(3)–C(4)	1.34(2)		
Bond angles, deg.			
Os(1)–Os(1)–Cl(1)	176.3(1)	O(1)–C(4)–O(3)	125(1)
Os(1)–Os(1)–O(1)	90.4(3)	O(2)–C(1)–O(4)	116(1)
Os(1)–Os(1)–O(2)	88.9(3)	O(1)–C(4)–C(5)	121(1)
Os(1)–Os(1)–O(3)	88.0(3)	O(3)–C(4)–C(5)	114(1)
Os(1)–Os(1)–O(4)	87.3(3)	O(2)–C(1)–C(2)	123(1)
Os(1)–O(1)–O(4)	119(1)	O(4)–C(1)–C(2)	121(1)
Os(1)–O(2)–C(1)	122(1)		
Os(1)–O(3)–C(4)	117.4(9)		
Os(1)–O(4)–C(1)	126(1)		

sense from that found for the butyrate, it appears unlikely that this deviation is chemically significant.

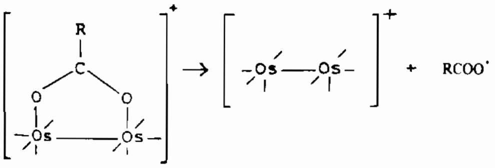
The coordination about each unique osmium atom is essentially octahedral and the mean Os–O distances of 2.009(7) Å in *1* and 2.014(10) Å in *2* are not significantly different. It was observed that the bridging ligands in the complexes $Os_2(hp)_4Cl_2 \cdot S$ were significantly distorted. However, in the butyrato complex no such distortion was found and none is found in the structures reported here. This may be rationalized in terms of there being little or no repulsive interaction between bridging and terminal ligands in the carboxylato compounds *1–3*. It may also be noted that the observed magnetic moment for $Os_2(hp)_4Cl_2 \cdot S$, 1.44 BM/Os at 300 K [4], is significantly greater than that found for the carboxylato complexes, 1.13–1.17 BM/Os at 300 K [4]. It is possible that greater population of states derived from configurations such as $\sigma^2\pi^4\delta^2\pi^{*2}$ or $\sigma^2\pi^4\delta^2\delta^*\pi^*$ weakens and lengthens the Os–Os bond in the $Os_2(hp)_4Cl_2$ molecule as compared to the $Os_2(O_2CR)_4Cl_2$ molecules. Further studies bearing on the relationship of structure to electronic configuration in these systems are in progress.

Mass Spectra

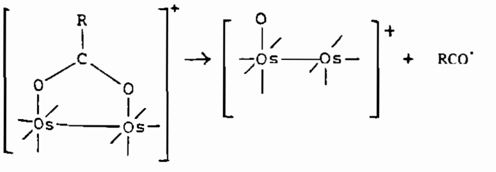
The diosmium compounds of general formula $Os_2(O_2CR)_4Cl_2$ give mass spectra in which the molecular ion is clearly observed. The natural occurrence of seven isotopes for osmium and the presence of two osmium atoms in the molecule leads to a molecular ion which gives nine different peaks with distinctive ratios. This pattern is a convenient fingerprint for any compound containing an Os_2^{n+} unit. The masses of ions quoted below will refer to the ion in which the total osmium mass is 380 amu.

For coordination compounds it has been demonstrated that prominent ions in their mass spectra are frequently associated with species having the metal ion in its most common oxidation state [10–17]. The data presented in Tables VI, VII and VIII indicate that for these diosmium compounds it is the oxidation states +2.5, +3.0 and +3.5 which are important.

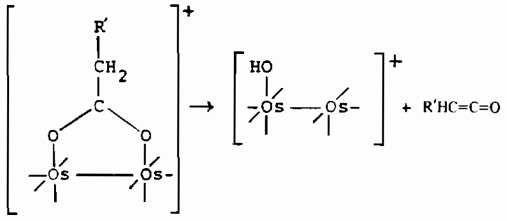
As reported previously fragmentation patterns due to the successive loss of two chloride ions were observed. In addition the loss of a variety of organic fragments was apparent. Three major pathways for fragmentation are evident (see eqns. 1, 2 and 3).



(1)



(2)



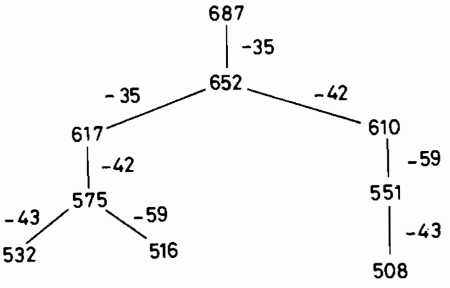
(3)

The loss of both chloride ions does not necessarily precede loss of organic moieties. On the contrary, it appears that the loss of one chlorine atom followed by ejection of a RCO• radical or RCH=C=O fragment is a favored process and in all the spectra the fragmentation pattern corresponding to the loss of two chloride ions from $[Os_2(O_2CR)_4Cl_2]^+$ is weak. It is also noteworthy that in none of the spectra was it possible to distinguish any discrete mononuclear osmium fragments.

The various fragmentation pathways are not independent of one another and the data presented in Tables VI–VIII indicate that none may succeed itself. For example, in the case of the acetate complex (Table VI) two successive or simultaneous losses of MeCOO•, MeCO• or $CH_2=C=O$ are not observed.

To an extent the failure of any one type fragmentation step to succeed itself may be viewed as a reflection of the narrow range of oxidation states available to the metal. The reactions shown in eqns. 1 and 2 result respectively in a reduction and an oxidation of the binuclear unit. These may not succeed

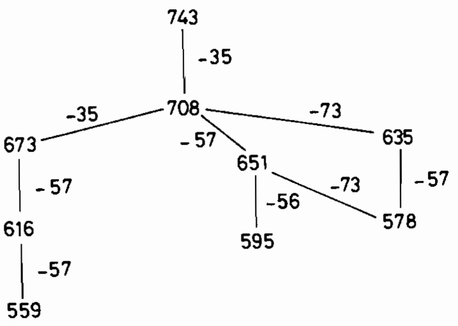
TABLE VI. The Mass Spectral Fragmentation Pattern of $Os_2(O_2CCH_3)_4Cl_2$.



m/e	Species	Ox. St. per Os
687	$Os_2Ac_4Cl_2^+$	3.5
652	$Os_2Ac_4Cl^+$	3.0
617	$Os_2Ac_4^+$	2.5
610	$Os_2Ac_3ClOH^+$	3.0
575	$Os_2Ac_3OH^+$	2.5
551	$Os_2Ac_2ClOH^+$	2.5
532	$Os_2Ac_2OOH^+$	3.0
516	$Os_2Ac_2OH^+$	2.0
508	$Os_2AcClOOH^+$	3.0

Ac = O_2CCH_3

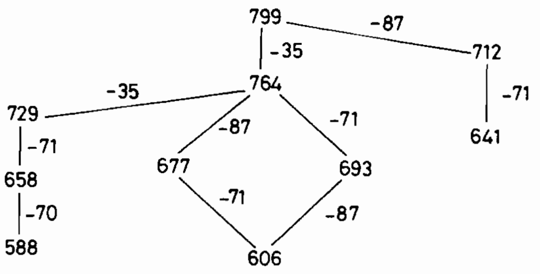
TABLE VII. The Mass Spectral Fragmentation Pattern for $Os_2(O_2CC_2H_5)_4Cl_2$.



m/e	Species	Ox. St. per Os
743	$Os_2Pr_4Cl_2^+$	3.5
708	$Os_2Pr_4Cl^+$	3.0
673	$Os_2Pr_4^+$	2.5
651	$Os_2Pr_3ClO^+$	3.5
635	$Os_2Pr_3Cl^+$	2.5
616	$Os_2Pr_3O^+$	3.0
595	$Os_2Pr_2ClOH^+$	2.5
578	$Os_2Pr_2ClO^+$	3.0
559	$Os_2Pr_2OO^+$	3.5

Pr = $O_2CC_2H_5$

TABLE VIII. The Mass Spectral Fragmentation Pattern of $Os_2(O_2C\text{-}n\text{-}C_3H_7)_4Cl_2$.



m/e	Species	Ox. St. per Os
799	$Os_2Bu_4Cl_2^+$	3.5
764	$Os_2Bu_4Cl^+$	3.0
729	$Os_2Bu_4^+$	2.5
712	$Os_2Bu_3Cl_2^+$	3.0
693	$Os_2Bu_3ClO^+$	3.5
677	$Os_2Bu_3Cl^+$	2.5
658	$Os_2Bu_3O^+$	3.0
641	$Os_2Bu_2Cl_2O^+$	3.5
606	$Os_2Bu_2ClO^+$	3.0
588	$Os_2Bu_2OOH^+$	3.0

Bu = $O_2CC_3H_7$

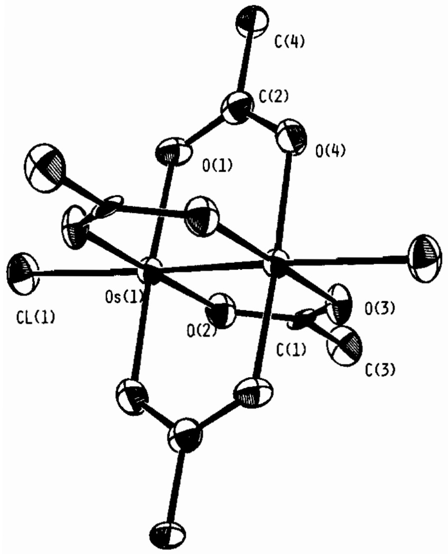


Fig. 1. An ORTEP drawing of the $Os_2(O_2CCH_3)_4Cl_2$ molecule, showing the atomic labeling scheme. Atoms are represented by their ellipsoids of thermal vibration scaled at the 50% probability level. There is an inversion center at the midpoint of the Os–Os′ bond.

themselves as this would lead to an unfavorable oxidation state, *i.e.*, one outside the range +2.5 to +3.5. The reaction shown in eqn. 3 leaves the oxidation state of the binuclear unit unchanged. The data contained in Tables VII and VIII are quite analogous to that pertaining to the acetate, in that the classes of fragments lost are identical, but the details of the analysis differ.

Interestingly, there is no evidence for the loss of carbon monoxide or carbon dioxide from any of these compounds although loss of the latter was the major fragmentation pathway for $Mo_2(O_2CH)_4$ [10].

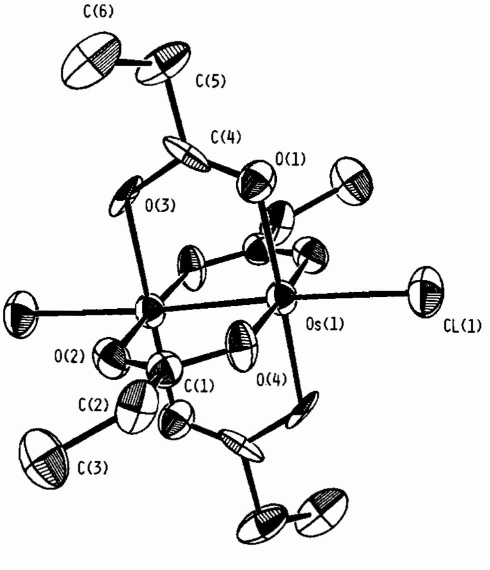


Fig. 2. An ORTEP drawing of the $Os_2(O_2CC_2H_5)_4Cl_2$ molecule, showing the atomic labeling scheme. Atoms are represented by their ellipsoids of thermal vibration scaled at the 50% probability level. There is an inversion center at the midpoint of the Os–Os′ bond.

Acknowledgements

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