$\begin{array}{l} Osmium(IV) \ Binuclear \ Nonelectrolytic \ Oxo-Bridged \\ Carboxylates. \ Molecular \ Structure \\ of \ [Os_2^{IV}(\mu \text{-}O)(\mu \text{-}O_2CCCl_3)_2Cl_4(PPh_3)_2] \cdot CH_2Cl_2 \end{array}$

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Abstract—The reactions between *trans*-[Os^{VI}O₂Cl₂L₂] (L = PPh₃, AsPh₃, SbPh₃) and carboxylic acids RCO₂H (R = CH₃, C(CH₃)₃, CH₂Cl, CCl₃, CF₃) are studied. The resulting binuclear compounds were found to have the general formula $[Os_2^{IV}(\mu-O)(\mu-O_2CR)_2Cl_4(L)_2]$ (L = PPh₃; R = CH₃, C(CH₃)₃, CH₂Cl, CCl₃, CF₃, and L = AsPh₃; R = CH₃, CH₂Cl, CCl₃, CCl₃, CF₃). X-ray diffraction analysis revealed that the $[Os_2^{IV}(\mu-O)(\mu-O_2CCCl_3)_2Cl_4(PPh_3)_2] \cdot CH_2Cl_2$ complex crystallizes in a triclinic system with space group $P\bar{1}$; *a* = 10.747(2) Å, *b* = 19.291(4) Å, *c* = 24.614(5) Å, α = 100.08(3)°, β = 90.63(3)°, γ = 97.05(3)°, *V* = 4983.5(17) Å³, *Z* = 4. The Os(μ -O)Os angle is 142.2(7)°. The interaction of *trans*-[Os^{VI}O₂Cl₂(SbPh₃)₂] with all the acids under study is attended by intramolecular redox reaction resulting in SbCl₂Ph₃.

The binuclear μ -oxocarboxylates containing the bent M₂(μ -O) metal core are of interest for researchers due to their structural conformity to some metal enzymes, such as hemerythrine, and due to their peculiar magnetic, spectral and redox properties [1, 2].

The Cr, Mn, Fe, V, Ti, and Ru complexes were synthesized and studied in [1–9], while investigations concerned with the diosmium complexes of this type were only reported in two papers [10, 11].

The first O-bridged osmium carboxylates with the OsOOs angle significantly deviating from 180° were synthesized by the authors of [10]. They showed that the complexes with the general formula $[Os_2^{IV}(\mu-O)(\mu-O_2CR)_2X_4\{PPh(R')_2\}_2]$ (R = CH₃, C₂H₅; X = Cl, Br; R' = Ph, Et) are formed when *trans*-[OsO₂X₂{PPh(R')₂}_2] is refluxed in a mixture of RCO₂H–(RCO)₂O under the inert atmosphere in the dark (in order to prevent the decomposition of the starting complex). The acetate complex $[Os_2^{IV}(\mu-O)(\mu-O_2CCH_3)_2Cl_4(PPh_3)_2]$ (C₂H₅)₂O (**I**) forms suitable crystals for X-ray diffraction analysis [10].

The results obtained in [11] make it possible to conclude that the binuclear O-bridged osmium carboxylates $[Os_2^{IV}(\mu-O)(\mu-O_2CR)_2Cl_4(L)_2]$ (R = CH₃, L = PPh₃, AsPh₃; R = CCl₃, L = PPh₃) are formed in the reaction of the corresponding *trans*-[OsO₂Cl₂L₂] with carboxylic acids under ordinary conditions (without using the inert atmosphere) and in the absence of (RCO)₂O. The formation, stability, and spectral properties of thus obtained compounds are substantially influenced by the nature of L in *trans*- $[OsO_2Cl_2L_2]$ and of R in the bridged carboxylates μ -RCO₂ [11].

The aim of this work was to study the reaction between *trans*- $[Os^{VI}O_2Cl_2L_2]$ (L = PPh₃, AsPh₃, SbPh₃) and carboxylic acids RCO₂H (R = CH₃, C(CH₃)₃, CH₂Cl, CCl₃, CF₃).

RESULTS AND DISCUSSION

When *trans*-[Os^{VI}O₂Cl₂L₂] (L = PPh₃, AsPh₃) is heated with liquid carboxylic acids (acetic or trifluoroacetic acids) or with solutions of solid carboxylic acids in benzene, dark brown diamagnetic binuclear osmium compounds are produced with the general formula $[Os_2^{IV}(\mu-O)(\mu-O_2CR)_2Cl_4(L)_2]$ (L = PPh₃; R = C(CH₃)₃, CH₃, CH₂Cl, CCl₃, CF₃, and L = AsPh₃; R = CH₃, CH₂Cl, CCl₃, CF₃). The yields of compounds increase with the increasing electron-accepting properties of R in carboxylic acids in the series CF₃ > CCl₃ > CH₂Cl > CH₃ > C(CH₃). The obtained compounds are stable in air, poorly soluble in water, ethanol, ether, saturated hydrocarbons, and limitedly soluble in acetonitrile; they are readily soluble in chloroform, dichloromethane, and benzene.

X-ray diffraction analysis of $[Os_2^{IV}(\mu-O)(\mu-O_2CCCl_3)_2Cl_4(PPh_3)_2] \cdot (CH_2Cl_2)$ (**II**) confirms bending of the Os₂(μ -O) core. The osmium atoms are bonded by two bridging trichloroacetate ions. Two chlorine atoms are in the *trans*-positions to the bridging oxygen atom



Fig. 1. Molecular structure of $[Os_2^{IV}(\mu-O)(\mu-O_2CCCl_3)_2Cl_4(PPh_3)_2] \cdot CH_2Cl_2$.

of the $Os_2(\mu$ -O). Two PPh₃ molecules lie opposite to the oxygen atoms of the bridging trichloroacetate groups (Fig. 1).

The comparison of the main bond lengths and angles in complexes II (Table 1) and I [10] indicates that an increase in the electron-accepting properties of R in the bridging carboxylate ligands leads to a slight decrease in the Os–(μ -O) and Os–Cl lengths and to an increase in the Os(μ -O)Os angle. At the same time, the donor capability of μ -O₂CCCl₃ is lower than that of μ -O₂CCH₃ and therefore, in complex II, the bonds Os–O with the bridging trichloroacetate ligands become longer. As a result, the Os…Os distance decreases, which brings about weak Os…Os interactions.

The elemental analysis and FAB mass spectroscopic data for the isolated osmium compounds $[Os_2^{IV}(\mu-O)(\mu-O_2CR)_2Cl_4(L)_2]$ (L = PPh₃; R = C(CH₃)₃, CH₃, CH₂Cl, CCl₃, CF₃, and L = AsPh₃; R = CH₃, CH₂Cl, CCl₃, CF₃) confirm that they contain the Os₂(μ -O)(μ -O₂CCH₃)₂ core. Given in Fig. 2 are the experimental and calculated $[Os_2O(O_2CCF_3)_2(PPh_3)_2Cl_2]^+$ fragments of FAB mass spectrum of the $[Os_2^{IV}(\mu-O)(\mu-O_2CCF_3)_2(L_2^{IV})_2]$.

Table 1. Selected bond lengths (Å) and angles (deg) in $[Os_2^{IV}(\mu-O)(\mu-O_2CR)_2Cl_4PPh_3)_2]^*$ complexes

Bond	R		Angle	R	
	CH ₃ **	CCl ₃ ***	Angle	CH3**	CCl ₃ ***
Os(1)–O(1)	1.830(10)	1.806(11)	Os(1)–P(1)	2.374(3)	2.369(6)
Os(2)–O(1)	1.828(9)	1.816(11)	Os(1)–O(2)	2.118(9)	2.161(13)
Os(1)– $Cl(1)$	2.306(4)	2.278(5)	Os(1)–O(5)	2.083(9)	2.101(15)
Os(1)–Cl(2)	2.332(4)	2.290(6)	Os…Os	3.440	3.427
Angle]	R			
	CH ₃ **	CCl ₃ ***			
Os(µ-O)Os	140.2(4)	142.2(7)			

* The atomic numbering corresponds to that in Fig. 1.

** The data of [10].

*** The data of this work.



Fig. 2. Isotopic ionic distribution for $[Os_2O(O_2CCF_3)_2(PPh_3)_2Cl_2]^+$ fragment $(m/z \ 1218)$ in $[Os_2^{IV}(\mu-O)(\mu-O_2CCF_3)_2Cl_4(PPh_3)_2]$ complex: (a) experimental, (b) calculated value.

The reactions of *trans*- $[Os^{VI}O_2Cl_2L_2]$ (L = PPh₃, AsPh₃) with all carboxylic acids under consideration afforded the Os binuclear complexes $[Os_2^{IV}(\mu-O)(\mu-O_2CR)_2Cl_4(L)_2]$ and white crystals. The results of the elemental analysis, IR data and the melting points indicated that these crystals are triphenylphosphine oxide (O=PPh₃) or triphenylarsine oxide (O=AsPh₃).

Thus, the formation of binuclear complexes $[Os_2^{IV}(\mu-O)(\mu-O_2CR)_2Cl_4(L)_2]$ (L = PPh₃, AsPh₃) can be described by the following redox reaction occurring in solution:

$$2[Os^{VI}O_2Cl_2L_2] + 2RCO_2H$$

$$\longrightarrow [Os_2^{IV}(\mu-O)(\mu-O_2CR)_2Cl_4L_2] + 2O=L + H_2O,$$

$$L = PPh_3, AsPh_3.$$

The reactions of *trans*- $[OsO_2Cl_2(SbPh_3)_2]$ with all the studied carboxylic acids always gave SbCl₂Ph₃ and the poorly soluble osmium-containing compounds of brown color. The formation of SbCl₂Ph₃ was confirmed by the elemental analysis and X-ray diffraction data [11].

The ratio Os : C in the osmium-containing products is close to 1 : 4 for R = CH₃, CH₂Cl, CCl₃, CF₃ and to 1 : 8 for R = C(CH₃)₃. The molar ratio Os : C for all samples under study suggests that the isolated products contain carboxylic acids. This is also confirmed by IR data. The spectral region 1400–1600 cm⁻¹ contains characteristic bands that can be assigned to v_{as} (COO) of the carboxyl groups of the corresponding carboxylic acids [12]. However, these bands are too broad and



Fig. 3. Molecular structure of trans-[Os(PPh₃)₂Cl₄].

have low intensity and therefore, they cannot be used for determination of the coordination mode of the RCO_2^- group.

Since the starting *trans*- $[Os^{VI}O_2Cl_2(SbPh_3)_2]$ complex is stable in air, one can suggest that in the reactions of carboxylic acids with *trans*- $[Os^{VI}O_2Cl_2(SbPh_3)_2]$, $SbCl_2Ph_3$ is likely to be eliminated due to a low stability of an intermediate Os compound. This suggestion is being verified now in our studies.

When trans-[Os^{VI}O₂Cl₂(PPh₃)₂] reacts with trimethvalcetic acid, the binuclear complex $[Os_2^{IV}(\mu-O)(\mu-O)]$ O₂CC(CH₃)₃)₂Cl₄(PPh₃)₂] forms in less than 30% yield. In this case, the main fraction of osmium-containing compound accounts for the mononuclear complex *trans*- $[Os^{IV}(PPh_3)_2Cl_4]$. This is confirmed by the results of the elemental analysis and X-ray diffraction study of this complex that forms dark brown needle-shaped crystals. The molecular structure of trans- $[Os^{IV}(PPh_3)_2Cl_4]$ is given in Fig. 3. The trans-[Os^{IV}(PPh₃)₂Cl₄] complex crystallizes in monoclinic system, space group $P2_1/n$; a = 9.324(2), b = 21.022(4), c = 9.603(2) Å, $\beta = 117.42(3)^{\circ}$, V = 1670.8(6) Å³, Z =2 (the main bond lengths Os(1)-Cl(1) 2.3008(16), Os(1)–Cl(2) 2.3249(16), Os(1)–P(1) 2.5195(17) Å and angles Cl(1a)Os(1)Cl(1) 180.0°, Cl(1a)Os(1)Cl(2)90.89(7)°, Cl(1)Os(1)Cl(2) 89.11(7)°, Cl(1)Os(1)Cl(2a) 90.89(7)°, Cl(2)Os(1)Cl(2a) 180.00(9)°, Cl(1)Os(1)P(1a) 92.62(6)°, Cl(2)Os(1)P(1a) 92.43(6)°, Cl(2a)Os(1)P(1a)



Fig. 4. IR spectrum of $[Os_2^{IV}(\mu-O)(\mu-O_2CCF_3)_2Cl_4(PPh_3)_2]$ in the region of the stretching vibrations $v_s(COO)$ and $v_{as}(COO)$ of the bridging carboxyl groups.

87.57(6)°, Cl(1*a*)Os(1)P(1) 92.62(6)°, Cl(1)Os(1)P(1) 87.38(6)°).

Unfortunately, IR method provides insufficient data in the case of binuclear Os(IV) μ -oxocarboxylates, and an accurate assignment of the bands typical of the stretching vibrations v_s (COO) and v_{as} (COO) of the bridging carboxyl groups is almost impossible. The range of 1440–1430 cm⁻¹, where vibrations v_s (COO) of carboxylate ligands usually appear [12], contains intense bands typical of the starting *trans*-[Os^{VI}O₂L₂Cl₂] (L = PPh₃, AsPh₃). The bands with maxima at 1500–1680 cm⁻¹ can be assigned to vibrations v_{as} (COO⁻) of the bridging carboxylate ions. However, these bands have very low intensity, which is not typical of μ -O₂CR.

IR spectrum of $[Os_2^{IV}(\mu-O)(\mu-O_2CCF_3)_2Cl_4(PPh_3)_2]$ (Fig. 4) exhibits a relatively intense band at 1622 cm⁻¹ that is likely to be due to vibrations $v_{as}(COO)$ of the bridging trifluoroacetate groups. The comparison of this band with the band corresponding to $v_{as}(COO)$ of the bridging acetate groups in $[Os_2^{IV}(\mu-O)(\mu-O_2CCH_3)_2Cl_4(PPh_3)_2]$ (observed by us at 1530 cm⁻¹ and at 1540–1525 cm⁻¹ in [10]) revealed the general tendency of shifting of the respective frequency in the trifluoroacetate complexes toward high-frequency region. The latter fact is characteristic of the bi- and trinuclear O-bridged trifluoroacetate complexes of Cr [13], Ru [14–16], and Rh [17–19].



Os₂O(O₂CCH₂Cl)₂(AsPh₃)₂Cl₄ complexes in CHCl₃. The electronic absorption spectra typical of the

 $[Os_2^{IV}(\mu-O)(\mu-O_2CR)_2Cl_4(L)_2]$ solutions in CHCl₃ are shown in Fig. 5. Those of the triphenylphosphine complexes $[Os_2^{IV}(\mu-O)(\mu-O_2CR)_2Cl_4(PPh_3)_2]$ in chloroform have the absorption band at 455–458 nm. In the spectra of the $[Os_2^{IV}(\mu-O)(\mu-O_2CR)_2Cl_4(AsPh_3)_2]$ complexes in CHCl₃, this intense band is shifted by 20–30 nm toward high frequencies (Fig. 5, Table 2).

If the diagram of MO energy levels for the osmium(IV) complexes with the linear configuration of the Os– μ -O–Os core [20, 21] is applied to the binuclear Os(IV) oxo-bridged carboxylate compounds with the Os(μ -O)Os angle deviating from 180°, the most intense band can be assigned then to the $\pi^{\text{nonb}} \longrightarrow \pi^*$ transition inside the Os₂(μ -O) core (Fig. 6).

Table 2 contains X-ray photoelectron spectroscopy data for the Os(IV) binuclear μ -oxocarboxylates. The binding energies for Os $4f_{7/2}$ (52.7–53.1 eV) and Cl $2p_{3/2}$ (198.6–199.0 eV) correlate with the data of [10, 21] and correspond to the formal oxidation state of osmium +4. The changes in X-ray photoelectron spectra do not make it possible to establish any general regularities and only reflect the result of the competing donation of the electron density of ligands L, chloride anions, and the bridging carboxylate groups.

EXPERIMENTAL

The starting *trans*-OsO₂Cl₂(PPh₃)₂ was prepared as described elsewhere [22], while *trans*-OsO₂Cl₂L₂ and $[Os_2^{IV}(\mu-O)(\mu-O_2CCH_3)_2Cl_4L_2]$ (L = AsPh₃, SbPh₃) we obtained using procedures [11].

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L	R	Electronic absorption spectra*	X-ray photoelectron spectra**, eV			
		$\begin{array}{c} \lambda_{max},nm \\ (\epsilon,l\;mol^{-1}\;cm^{-1}) \end{array}$	Os 4f _{7/2}	P 2p _{3/2}	As 3d	Cl 2p _{3/2}
PPh ₃	C(CH ₃) ₃	456 (10300)	52.7	132.3		198.6
	CH ₃	456 (10100)	52.8	133.4		199.0
	CH ₂ Cl	458 (17300)	53.1	132.3		199.3
	CCl ₃	455 (13600)	53.0	132.6		198.8
	CF ₃	455 (10400)	52.6	132.0		199.0
AsPh ₃	CH ₃	426 (7400)	52.9		44.6	198.9
	CH ₂ Cl	434 (11500)	53.0		44.5	199.0
	CCl ₃	426 (11400)	52.8		44.6	198.6
	CF ₃	425 (12000)	52.8		44.6	198.8

Table 2. X-ray photoelectron and electronic absorption spectra of Os μ -oxocarboxylates $[Os_2^{IV}(\mu-O)(\mu-O_2CR)_2Cl_4(L)_2]$

* The spectra were recorded in chloroform.

** The spectra are normalized in terms of the binding energy of electrons of the C1s line taken as 285.0 eV.

 $[Os_{2}^{IV}(\mu - O){\mu - 0}]$ **Synthesis** of $O_2CC(CH_3)_3$ $Cl_4(PPh_3)_2$. A suspension of trans- $[OsO_2(PPh_3)_2Cl_2]$ (1 g) in 20 ml of C(CH₃)_3CO₂H (4 g) in chloroform was heated with reflux condenser until the starting complex dissolved completely. After the unreacted *trans*-[Os^{VI}O₂(PPh₃)₂Cl₂] was filtered off, the excess solvent was distilled off from the reaction mixture, whereas pivalic acid excess was removed by sublimation. The remaining solid was dissolved in chloroform and the targeted product was salted out with hexane. The complex was dried in a vacuum desiccator over potassium hydroxide. The yield was ~30%. The complex is insoluble in water, alcohols, limitedly soluble in acetonitrile, and readily soluble in halogen-sub-



Fig. 6. Energy levels of MO for Os(IV) O-bridged carboxylate complexes.

stituted hydrocarbons or arenes.

For $C_{46}H_{48}Cl_4O_5Os_2P_2$ anal. calcd. (%): Os, 19.04; C, 43.27; Cl, 7.10. Found (%): Os, 18.9; C, 43.5; Cl, 8.0.

FAB (*m*/*z*): 1231 [M–Cl]⁺. IR (v, cm⁻¹): 443 w, 553 s, 619 w, 691 s, 744 m, 997 w, 1028 w, 1092 m, 1159 w, 1220 w, 1408 w, 1435 s, 1482 m, 1698 m, 2927 w, 2965 w, 3059 w, 3440 b.

Synthesis of $[Os_2^{IV}(\mu-O)(\mu-O_2CCH_2Cl)_2Cl_4(PPh_3)_2]$. A suspension of $[OsO_2(PPh_3)_2Cl_2]$ (1.5 g) in 20 ml of CH_2ClCO_2H (5 g) in chloroform was heated with reflux condenser until the starting complex dissolved. The excess solvent was distilled off from the reaction mixture; the remaining solid containing the complex and monochloroacetic acid was suspended in cold water. This aqueous solution was decanted and this procedure was repeated to get neutral reaction of washing water. The complex was filtered off and dired in a vacuum desiccator over silica gel to a constant weight. The complex yield was ~90%.

FAB (*m*/*z*): 1215 [M–Cl]⁺. IR (v, cm⁻¹): 524 s, 691 s, 747 m, 798 w,997 w, 1094 m, 1121 m, 1191 s, 1258 m, 1399 m, 1433 m, 1483 w, 1561 s, 2924 w, 3058 w, 3442 b.

Synthesis of $[Os_2^{IV}(\mu-O)(\mu-O_2CCCl_3)_2Cl_4(PPh_3)_2]$

was carried out similarly to that of $[Os_2^{IV}(\mu-O)(\mu-O_2CCH_2Cl_2Cl_4(PPh_3)_2]$. The yield was ~95%.

For C₄₀H₃₀Cl₁₀O₅Os₂P₂

anal. calcd. (%):	Os, 27.42;	C, 34.62;	Cl, 25.55.
Found (%):	Os, 26.9;	C, 35.2;	Cl, 24.6.

FAB (*m*/*z*): 1351 [M–Cl]⁺. IR (v, cm⁻¹): 518 w, 610 b, 682 s, 718 w, 743 s, 820 w, 847 m, 1340 w, 1430 w, 1500 w, 1605 w.

The needle-shaped crystals are formed on slow evaporation of the complex solution in methylene chloride. The complex cocrystallizes with one CH₂Cl₂ mol-

ecule. The crystals are triclinic, space group $P\bar{1}$; a = 10.747(2) Å, b = 19.291(4) Å, c = 24.614(5) Å, $\alpha = 100.08(3)^{\circ}$, $\beta = 90.63(3)^{\circ}$, $\gamma = 97.05(3)^{\circ}$, V = 4983.5(17) Å³, Z = 4.

Synthesis of $[Os_2^{IV}(\mu-O)(\mu-O_2CCF_3)_2Cl_4(PPh_3)_2]$. A sample of *trans*- $[OsO_2Cl_2(PPh_3)_2]$ (1 g) was boiled with excess CF₃CO₂H (20 ml) in a flask with reflux condenser for 2 h. The excess solvent was distilled off, and the dry residue was dissolved in chloroform. The target product was precipitated with hexane. The complex was dried in a vacuum desiccator over KOH to a constant weight. The obtained dark brown compound is insoluble in water or alcohol; limitedly soluble in acetone, and readily soluble in ether, chloroform, or benzene. The yield was ~80%.

For $C_{40}H_{30}Cl_4F_6O_5Os_2P_2$					
anal. calcd. (%):	Os, 29.52;	C, 37.28;	Cl, 11.00.		
Found (%):	Os, 29.3;	C, 37.8;	Cl, 12.2.		

FAB (m/z): 1255 $[M-Cl]^+$, 1177 $[M-O_2CCF_3]^+$. IR (v, cm⁻¹): 432 m, 523 s, 691 s, 731 m, 860 w, 999 w, 1094 m, 1153 m, 1196 s, 1385 w, 1436 m, 1485 w, 1622 m, 2854 w, 2925 w, 3059 w, 3440 b.

Synthesisof $[Os_2^{IV}(\mu-O){\mu-O_2CC(CH_3)_3}_2Cl_4(AsPh_3)_2]$ was performed similarlyto that of $[Os_2^{IV}(\mu-O){\mu-O_2CC(CH_3)_3}_2Cl_4(PPh_3)_2].$ The yield of dark brown complex was ~50%.

For C46H48As2Cl4O5Os	2	
anal. calcd. (%):	Os, 28.12;	Cl, 10.48.
Found (%):	Os, 27.6;	Cl, 9.8.

FAB (m/z): 1318 [M–Cl]⁺. IR $(v, \text{ cm}^{-1})$: 472 s, 690 s, 740 s, 778 w, 850 b, 1000 w, 1028 w, 1085 s, 1163 b, 1187 b, 1440 s, 1490 w, 1630 s, 3420 b.

Synthesis of $[Os_2^{IV}(\mu-O)(\mu-O_2CCH_3)_2Cl_4(AsPh_3)_2]$. This complex was synthesized by the same procedure as the $[Os_2^{IV}(\mu-O)(\mu-O_2CCF_3)_2Cl_4(PPh_3)_2]$ complex. The dark brown complex was obtained in the yield of ~70%.

For $C_{40}H_{36}O_5As_2Cl_4As_2Cl_4As_2Cc_4As_2Cc_4As_2Cc_4As_2Cc_4As_2Cc_4As_2Cc_4As_2Cc_4As_2Cc_4As_2Cc_4As_2C$	Ds_2	
anal. calcd. (%):	Os, 30.0;	Cl, 11.2.
Found (%):	Os, 29.8;	Cl, 11.4.

FAB (*m*/*z*): 1235 [M–Cl]⁺. IR (v, cm⁻¹): 472 s, 690 s, 740 s, 778 w, 850 b, 1000 w, 1028 w, 1085 s, 1163 b, 1187 b, 1440 s, 1490 w, 1630 s, 3420 b.

 $[Os_2^{IV}(\mu-O)(\mu-O_2CCH_2Cl)_2Cl_4(AsPh_3)_2]$ was synthesized using the same procedure as in the case of the $[Os_2^{IV}(\mu-O)(\mu-O_2CCH_2Cl)_2Cl_4(PPh_3)_2]$ complex. The yield was ~75%.

For C₄₀H₃₄As₂Cl₆O₅Os₂

anal. calcd. (%):	Os, 28.44;	C, 35.91;	Cl, 15.90.
Found (%):	Os, 27.8;	C, 36.6;	Cl, 14.3.

FAB (*m*/*z*): 1303 [M–Cl]⁺. IR (v, cm⁻¹): 471 m, 544 w, 691 s, 739 s, 810 m, 841 m, 997 w, 1025 w, 1082 m, 1188 m, 1258 m, 1311 m, 1397 s, 1438 vs, 1481 m, 1561 m, 2854 w, 2925 w, 3055 w, 3442 b.

 $[Os_2^{IV}(\mu-O)(\mu-O_2CCCl_3)_2Cl_4(AsPh_3)_2]$ was synthesized similarly to that of $[Os_2^{IV}(\mu-O)(\mu-O_2CCH_2Cl)_2Cl_4(PPh_3)_2]$. The yield of the complex was ~90%.

FAB (m/z): 1439 [M–Cl]⁺. IR $(v, \text{ cm}^{-1})$: 471 m, 687 vs, 741 vs, 845 m, 998 w, 1025 w, 1082 w, 1188 w, 1274 m, 1343 m, 1437 s, 1481 w, 1617 w, 2855 w, 2924 w, 3055 w, 3441 b.

Synthesis of $[Os_2^{IV}(\mu-O)(\mu-O_2CCF_3)_2Cl_4(AsPh_3)_2]$ was carried out using the same procedure as in the case of $[Os_2^{IV}(\mu-O)(\mu-O_2CCF_3)_2Cl_4(PPh_3)_2]$. The complex was obtained in ~(60–70)% yield.

For $C_{40}H_{30}As_2Cl_4F_6O_5Os_2$ anal. calcd. (%): Os, 27.63; C, 34.90; Cl, 10.30. Found (%): Os, 26.9; C, 35.2; Cl, 9.3.

FAB (m/z): 1343 [M–Cl]⁺. IR $(v, \text{ cm}^{-1})$: 471 m, 620 w, 690 s, 737 s, 789 w, 839 w, 1082 m, 1196 vs, 1388 w, 1437 m, 1481 w, 1625 m, 2924 w, 3057 w, 3449 b.

The electronic absorption spectra of solutions of the complexes were recorded on a SF-56 spectrophotome-

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ter in the range of 190–1100 nm in quartz cells with l = 1 cm. IR spectra in the range of 4000–400 cm⁻¹ were taken on a Nicolet FT-360 spectrophotometer (with KBr pellets); FAB mass spectra were recorded on a Trio2000 mass spectrometer in the region of positively charged ions by bombarding 3-nitrobenzyl alcohol matrices with xenon atoms.

X-ray photoelectron spectra were measured on a Perkin-Elmer PHI 5400 electron spectrophotometer with Mg K_{α} source. The powdered samples were pressed in indium and after preliminary evacuation were placed on a manupulator cooled with liquid nitrogen. The working vacuum in spectrometer was 10^{-8} mmHg.

X-ray diffraction analysis¹ was carried out on a four-circle automated Syntex $P2_1$ diffractometer. The elemental analysis of the complexes for C was performed on a Perkin-Elmer 2400 CHN analyzer; Os was determined gravimetrically after the complexes were reduced in a flow of hydrogen; Cl was found by potentiometrical titration with silver ions of solutions of cakes of the complexes with excess potassium carbonate in a 10% nitric acid.

Peaks of molecular masses were calculated using polynomial expansion based on the natural isotope abundance with IsoPro [23] and Molecular Weight Calculator [24] programs.

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REFERENCES

- 1. Kurtz, D.M.J., Chem. Rev., 1990, vol. 90, no. 2, p. 585.
- Feig, A.L. and Lippard, S.J., *Chem. Rev.*, 1994, vol. 94, no. 3, p. 759.
- 3. Weldon, V.T., Wheeler, D.E., Kipby, J.P., *et al.*, *Inorg. Chem.*, 2001, vol. 40, no. 26, p. 6809.

- 4. Knopp, P. and Wieghardt, K., *Inorg. Chem.*, 1991, vol. 30, no. 21, p. 4061.
- Tanase, T. and Lippard, S.J., *Inorg. Chem.*, 1995, vol. 34, no. 18, p. 4682.
- Bond, M.R., Czernuszewicz, R.S., Dave, B.C., et al., Inorg. Chem., 1995, vol. 34, no. 23, p. 5857.
- Bernard, E., Chardon-Noblat, S., and Deronzier, A., Inorg. Chem., 1999, vol. 38, no. 1, p. 190.
- 8. Tanase, T., Takeshita, N., Inoue, C., *et al.*, *J. Chem. Soc., Dalton Trans.*, 2001, no. 15, p. 2293.
- 9. Abe, M., Mitani, A., Ohsawa, A., et al., Inorg. Chim. Acta, 2002, vol. 331, p. 158.
- 10. Armstrong, J.E., Robinson, W.R., and Walton, R.A., Inorg. Chem., 1983, vol. 22, no. 9, p. 1301.
- Belyaev, A.N., Eremin, A.V., Simanova, S.A., *et al.*, *Zh. Prikl. Khim. (S.-Peterburg)*, 2002, vol. 75, no. 12, p. 1947.
- 12. Nakomoto, K., Infrared and Raman Spectra of Inorganic and Coordination Compounds, Chichester: Wiley, 1986.
- 13. Belyaev, A.N., Simanova, S.A., Matasov, V.B., *et al.*, *Zh. Prikl. Khim.* (*S.-Peterburg*), 1998, vol. 71, no. 9, p. 1417.
- 14. Neubold, P., Wieghardt, K., Nuber, B., et al., Inorg. Chem., 1989, vol. 28, no. 3, p. 459.
- 15. Belyaev, A.N., Simanova, S.A., Eremin, A.V., *et al.*, *Zh. Prikl. Khim.* (*S.-Peterburg*), 1995, vol. 68, no. 1, p. 76.
- Belyaev, A.N., Simanova, S.A., Eremin, A.V., *et al.*, *Zh. Prikl. Khim.* (S.-Peterburg), 1998, vol. 71, no. 12, p. 1975.
- Belyaev, A.N., Simanova, S.A., Gorlov, M.Yu., *et al.*, *Zh. Prikl. Khim.*(*S.-Peterburg*), 1998, vol. 71, no. 12, p. 1971.
- Belyaev, A.N., Simanova, S.A., Gorlov, M.Yu., *et al.*, *Zh. Prikl. Khim.*(*S.-Peterburg*), 2000, vol. 73, no. 11, p. 1778.
- 19. Belyaev, A.N., Simanova, S.A., Gorlov, M.Yu., *et al.*, *Zh. Obshch. Khim.*, 2000, vol. 71, no. 8, p. 1259.
- 20. San Filippo, J., Jr., Fagan, P.J., and Di Salvo, F.J., *Inorg. Chem.*, 1977, vol. 16, no. 5, p. 1016.
- 21. Imbe, Y., Umakoshi, K., Matsunami, C., et al., Inorg. Chem., 1995, vol. 34, no. 4, p. 813.
- 22. Salmon, D.J. and Walton, R.A., *Inorg. Chem.*, 1978, vol. 17, no. 9, p. 2379.
- 23. IsoPro. Version. 3.0, http://members.aol.com/msmssoft/.
- 24. Molecular Weight Calculator. Version. 6.22. Build 171, http://www.alchemistmatt.com.

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