Binuclear Osmium μ -Oxocarboxylate Complexes [Os₂(μ -O)(μ -O₂CR)₂Cl₄L₂] (R = CH₃, CCl₃; L = PPh₃, AsPh₃) and Their Electrochemical Behavior in Dichloromethane

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Abstract—Cyclic voltammetry and galvanostatic coulometry techniques were used to determine how the redox properties of osmium binuclear μ -oxocarboxylates [Os₂^{IV}(μ -O)(μ -O₂CR)₂Cl₄L₂] (R = CH₃, CCl₃; L = PPh₃ and R = CH₃; L = AsPh₃) are influenced by the nature of the bridging carboxylate ligand RCOO⁻ and ligand L. It was shown that all compounds in solution of dichloromethane undergo two single-electron reduction processes. The data obtained were compared with the DFT calculations of the electronic structure of the model complexes [Os₂^{IV}(μ -O)(μ -O₂CR)₂Cl₄L₂] (R = CH₃, CCl₃; L' = PH₃ and R = CH₃; L' = AsH₃).

The osmium compounds with the Os– $(\mu$ -O)–Os core are poorly studied, although the fist structurally characterized complex Cs₄[Os₂(μ -O)Cl₁₀] was reported as far as in 1973 [1]. Only four papers devoted to the osmium compounds of this class were published for the last 30 years [2–5].

X-ray diffraction data reported in [3, 5] indicate that the nature of ligand L in the starting mononuclear compound, i.e., the *trans*-[OsO₂X₂L₂] (X = Cl, Br), determines the formation of a linear or a bent binuclear Os– O–Os fragment. If L = PPh₃ or PEt₂Ph in the initial complex, then the $[Os_2^{IV}(\mu-O)(\mu-O_2CR)_2Cl_4L_2]$ complexes (R = CH₃, C₂H₅; X = Cl, Br) are formed with the bent metal-containing Os₂(μ -O) core and the bidentate coordination of two bridging carboxylate groups [3]. In the case where pyridine (Py) is a ligand, the $[(Py)_2Cl_2(CH_3COO)Os(\mu-O)Os(Py)_2Cl_3]$ compounds are formed with the linear Os₂(μ -O) core and a single acetate group coordinated in the monodentate mode [5]

The aim of this work was to study the effect of the nature of the R group in the bridging carboxylate ligand RCOO⁻ and ligand L in the osmium binuclear μ -oxocarboxylates [Os₂^{IV}(μ -O)(μ -O₂CR)₂Cl₄L₂] (R = CH₃, L = PPh₃ (I); R = CH₃, L = AsPh₃ (II), and R = CCl₃, L = PPh₃ (III)) on their electrochemical behavior. We selected and used PPh₃ and AsPh₃ as ligands because, on the one hand, they act as donors and have free electron pair, and, on the other hand, they have unoccupied *d* orbitals with sufficiently low energies, unlike the pyridine ligand.

EXPERIMENTAL

The electrochemical behavior of complexes I-III was studied by cyclic voltammetry (CV) and galvanostatic coulometry (GC) methods at $T = 20 \pm 2^{\circ}$ C using a PI-50-1.1 potentiostat, a PR-8 programmer, the twocoordinate XY 4130 Recorder. The experiments were conducted in a glass (pyrex) three-electrode cell. The platinum wire with a surface 22.6 mm² served as a working electrode in CV study and the platinum grid was used as the working electrode in GC measurements. The reference electrode was Ag|0.01 M AgNO₃, $0.1 \text{ M} [(n-\text{Bu})_4\text{N}]\text{ClO}_4, \text{CH}_2\text{Cl}_2$. Nickel plates were used as the auxiliary electrodes. The working electrode compartment was partitioned from the reference electrode and auxiliary electrode compartments by discharge cocks. A 0.1 M $[(n-Bu)_4N]$ ClO₄ solution saturated with argon was used as a supporting electrolyte, the concentrations of complexes were 1-5 and 5 mol/l for CV and GC studies, respectively. The cyclic voltammograms were recorded at the potential sweep rate 100 mV/s.

The electronic absorption spectra of solutions of the complexes in chloroform were recorded on a SF-56 spectrophotometer in the range of 200–1100 nm in quarts cells with l = 1 cm.

IR spectra were taken in the range of 400–4000 cm⁻¹ using a Nicolet FT-360 spectrophotometer with KBr pellets.

X-ray photoelectronic spectra were recorded on a Perkin-Elmer PHI 5400 spectrophotometer with excitation by X-ray radiation. The powdered samples were pressed in indium, evacuated, and placed on manipulator cooled with liquid nitrogen. The operating vacuum in spectrophotometer was 10^{-8} mmHg.



Fig. 1. The structure of binuclear Os(IV) oxocarboxylate complex with the $[Os_2(\mu-O)(\mu-O_2CCCl_3)_2]^{4+}$ core (phenyl rings are not shown for clarity).

The binuclear Os μ -oxocarboxylates $[OsOs_2^{IV}(\mu-O)(\mu-O_2CR)_2Cl_4(PPh_3)_2]$ ($R = CH_3$ (I) and $R = CCl_3$ (III)) were synthesized following the procedure we previously described in [6].

The $[Os_2(\mu-O)(\mu-O_2CCH_3)_2Cl_4(AsPh_3)_2]$ complex (II) was prepared by boiling a suspension of 1 g of the trans-[OsO₂(AsPh₃)₂Cl₂] in 20 ml of glacial acetic acid until the initial complex dissolved completely. In this case, the colorless solution became dark brown. A solid residue, formed after evaporating the solution on air bath, was dissolved in 40 ml of chloroform, and a small amount of pentane was added to the obtained solution. The precipitated complex was filtered off, washed with ether, and kept in a desiccator over KOH to a constant weight. Then it was dissolved in minimum quantity of chloroform and purified on a chromatographic column (silipore 600 (GC), 0.125-0.160 mm). The solution was concentrated at room temperature, and a solid residue was kept in vacuum-desiccator to a constant weight. The product yield was ~70%. Complex II has dark brown color, is readily soluble in chloroform, dichloromethane, and benzene.

For C ₄₀ H ₃₆ As ₂ Cl ₄ O ₅ Os ₂						
Anal. calcd. (%):	Cl, 11.2;	Os, 30.0.				
Found (%):	Cl, 11.4;	Os, 29.8.				

IR spectrum, 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. Electronic absorption spectrum, λ_{max} , nm (ϵ , 1 mol⁻¹ cm⁻¹): 426 (7362).



Fig. 2. CV of a 1 mM solution of $[Os_2(\mu-O)(\mu-O_2CCCl_3)_2Cl_4(PPh_3)_2]$ in CH₂Cl₂ (with a 0.1 M solution of $[(n-Bu)_4N]ClO_4$ in CH₂Cl₂ as a supporting electrolyte and a potential sweep rate 100 mV/s).

RESULTS AND DISCUSSION

X-ray data for complex **III** showed that the $Os_2(\mu$ -O) fragment¹ is bent. The osmium atoms are bonded by two bridging trichloroacetate ions. Two chlorine atoms are in the *trans*-positions with respect to the bridging oxygen atom of the $Os_2(\mu$ -O) core. Two PPh₃ molecules lie opposite to the oxygen atoms of the bridging trichloroacetate groups (Fig. 1).

A typical CV curve for complex **III** is shown in Fig. 2, while the galvanostatic chronopotentiogram of the complex **III** reduction is given in Fig. 3.

The comparison of the CV and GC results for solutions of complexes **I–III** in dichloromethane makes it possible to conclude that these compounds undergo two subsequent single-electron reduction processes (n = 0.97-1.02).

$$[Os_{2}^{IV}(\mu-O)(\mu-O_{2}CR)_{2}Cl_{4}L_{2}] + e^{-}$$

$$= [Os_{1}^{III}Os_{1}^{IV}(\mu-O)(\mu-O_{2}CR)_{2}Cl_{4}L_{2}]^{-},$$
(1)

$$[Os^{III}Os^{IV}(\mu-O)(\mu-O_2CR)_2Cl_4L_2]^{-} + e^{-}$$

=
$$[Os_2^{III}(\mu-O)(\mu-O_2CR)_2Cl_4L_2]^{2-}.$$
 (2)

The first process is reversible, while the second one is irreversible in both electrochemical ($\Delta E_p \ge 56$ mV at 20°C) and chemical ($i_{p,c}/i_{p,a} \ge 1$) aspects (where ΔE_p is the potential difference between the anode and cathode

 $^{1} \text{ The } [\text{Os}_{2}^{IV}(\mu\text{-O})(\mu\text{-O}_{2}\text{CCCl}_{3})_{2}\text{Cl}_{4}(\text{PPh}_{3})_{2}] \cdot \text{CH}_{2}\text{Cl}_{2} \text{ complex crys-}$

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tallizes in triclinic system: space group $P\bar{1}$; a = 10.747(2), b = 19.291(4), 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; R = 0.0389. The Os-(μ -O)–Os angle is 142.2(7)° [7].



Fig. 3. Galvanostatic chronopotentiogram of a 5 mM solution of $[Os_2(\mu-O)(\mu-O_2CCCl_3)_2Cl_4(PPh_3)_2]$ in CH_2Cl_2 (with 0.15 mA current).

peaks; $i_{p,c}$ is the reduction peak current, $i_{p,a}$ is the oxidation peak current (Table 1).

As follows from the voltammetry data, the potentials of the reduction processes (1) and (2) are mainly determined by the nature of R in the bridging carboxylate ligand. Thus, the half-wave potentials $(E_{1/2})$ of these processes for the trichloroacetate complex III are more positive as compared to the respective values for the acetate analogue I (Table 1). At the same time, the potential stability regions ($\Delta E_{1/2}$) of the mixed-valence form $[Os^{III}Os^{IV}(\mu-O)(\mu-O_2CR)_2Cl_4(PPh_3)_2]^-$ are almost the same for complexes III and I (Table 1). On the contrary, the triphenylarsinic complex II has more narrow region of thermodynamic stability of the mixed-valence form as compared to those of the triphenylphosphine complexes I and III. The calculated coproportionation constants $K_{coprop} = \exp(\Delta E_{1/2}F/RT)$ correspond to the following process

$$Os_2^{IV} + Os_2^{III} \implies 2Os^{III}Os^{IV}$$

and are equal to 6.2×10^{17} and 3.4×10^{18} for triphenylphosphine complexes I and III, respectively and 1.1×10^{14} for the triphenylarsinic derivative II.

In order to reduce the basis, the calculations of the electronic structure of $[Os_2(\mu-O)(\mu-O_2CCH_3)_2L_2Cl_4]$ were performed using the model systems, where L' = PH₃, AsH₃ were used instead of L. These calculations were carried out by the B3LYP DFT method in the 6-31G** basis for the H, C, O, P, Cl, atoms and with HW

pseudopotential for the As and Os atoms [8] using GAMESS-2001 program package [9].

To estimate the difference in the strength of the metal-carboxylate ligand bonds, the binding energies (BE) were calculated from the differences of the total energies of the compounds undergoing dissociation: $[Os_2(\mu-O)(\mu-OOCR)_2(PH_3)_2Cl_4]$ $[Os_2(\mu-O)(PH_3)_2Cl_4]^{2+} + 2RCOO^{-}$. In the complexation of Os with carboxylates, the change in the electron density (Δq) for CH₃COO⁻ (0.651 e) is higher than for CCl_3COO^- (0.545 e), and the value of BE in the complex is also higher for the acetate anion (950 kJ/mol) as compared to the trichloroacetate anion (809 kJ/mol). The Mulliken redistribution of the electron density in the course of complexation in a series of carboxylates under study resulted in the charges on the Os atoms (q)that are in a good agreement with the BE ($Os4f_{7/2}$), which follows from X-ray photoelectronic spectroscopy: q = 0.616 e, Os4 $f_{7/2} = 52.8 eV (R = CH_3) < q = 0.626 e$, Os4 $f_{7/2} = 53.0 (R = CCl_3)$.

The replacement of the phosphine ligand by the arsine ligand causes only insignificant reduction in the energy of binding of the bridging acetate ligand with the coordinated $[Os_2(\mu-O)L'_2 Cl_4]^{2+}$ fragment (948 kJ/mol).

The pattern of the electron density redistribution obtained for the model complexes under consideration cannot be directly applied to the compounds with PPh₃ and AsPh₃. The reason for this is that the energy of ionization (I) of phosphine is higher than that of arsine while the respective triphenyl derivatives exhibit the reverse situation $I_{\text{PPh}_3} < I_{\text{AsPh}_3}$ (Table 2). At the same time, insignificant differences in the I values and in the electron affinity (A) (Table 2) calculated for these ligands make it possible to assume that these ligands have close donor-acceptor properties and similar electronic structures of acetates $[Os_2(\mu - O)(\mu O_2CCH_3)_2L_2Cl_4].$

Thus, the quantum-chemical calculations provide grounds to believe that the increased charge on the Os atoms due to the weaker electron-donor properties of the trichloroacetate ligands [11] can be the reason for the higher $E_{1/2}$ values of the electrode processes (1) and

Table 1. Voltammetry characteristics for Os binuclear complexes I-III*

Complex		s ^{III} Os ^{IV}	Os ^{III} Os	$^{\rm IV}/{\rm Os}_2^{\rm III}$	$\Delta E_{1/2}, \mathbf{V}$
	$E_{1/2}(\Delta E_p), \mathrm{mV}$	$i_{p.c}/i_{p.a}$	$E_{1/2}(\Delta E_p), \mathrm{mV}$	$i_{p.c}/i_{p.a}$	
I	-23(65)	0.9	-1058(115)	1.7	1.035
II	-28(58)	1.0	-845(110)	2.0	0.817
III	313(65)	1.0	-765(120)	1.0	1.078

* $E_{1/2} = (E_{p.a} + E_{p.c})/2$, $\Delta E_p = E_{p.a} - E_{p.c}$ and $\Delta E_{1/2} = E_{1/2}(Os_2^{IV}/Os_1^{III}Os_1^{IV}) - E_{1/2}(Os_1^{III}Os_2^{IV}/Os_2^{III})$.

Table 2. The calculated (I_{calcd}) and experimental (I_{exp}) [10] ionization energies and electron affinities for ligands L and L'

L and L'	I _{exp}	Icalcd	Α	
	eV			
PH ₃	10.60	10.57	-2.57	
AsH ₃	10.51	10.29	-2.75	
PPh ₃	7.85	7.50	-0.62	
AsPh ₃	8.03	7.67	-0.71	

(2) for the trichloroacetate complex **III** as compared to the acetate complexes **I** and **II**.

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