Synthesis and Reaction of the Novel Complex $[AsPh_4][OsCl_5(H_2O)]$. X-ray Structure Analysis of $[AsPh_4][OsCl_5(H_2O)]\cdot 2EtOH$ and $[AsPh_4][OsCl_5(EtOH)]\cdot EtOH$

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Received January 26, 2000

The synthesis and characterization of the anionic mononuclear and homobinuclear osmium complexes $[AsPh_4][OsCl_5L]\cdot x$EtOH [L = H_2O, $x = 2$ (**9**); L = EtOH, $x = 1$ (**10a**); L = py, $x = 0$ (**10b**)] and $[AsPh_4]_2[Cl_5Os(pyz)OsCl_5]$ (**12**) (pyz = pyrazine) are described. Upon reduction in a chloride-containing medium, OsO_4 (**1**) affords the osmium(IV) species $[OsCl_5(H_2O)]^-$ (**2**), which could be isolated by extraction with *n*-tributyl phosphate (TBP). Complex **9** is the first fully characterized chloroaquo complex of Os(IV). This complex is an effective starting material for the preparation of novel species, such as **10a**, **10b**, and **12**. The X-ray structures of **9** and **10a** were determined. Both compounds crystallize in the monoclinic space group $P2_1/n$. **9**: $C_{28}H_{34}AsCl_5O_3Os$, $a = 10.910(4)$ Å, $b = 17.127(5)$ Å, $c = 17.555(7)$ Å, $\beta = 103.77(2)°$, $V = 3186(2)$ Å^3, and $Z = 4$. **10a**: $C_{28}H_{32}AsCl_5O_2Os$, $a = 10.7762(2)$ Å, $b = 17.3939(1)$ Å, $c = 17.1477(3)$ Å, $\beta = 103.645(1)°$, $V = 3123.45(8)$ Å, and $Z = 4$. Complexes **9** and **10a** crystallize with two and one molecule of EtOH and are bonded via hydrogen bridges to the H_2O and EtOH ligand in **9** and **10a**, respectively.

Introduction

$[OsCl_6]^{2-}$ is a well-established and characterized complex anion. The reaction chemistry of this transition metal ion is dominated by ligand-exchange reactions.[1] This process is only observed when the incoming molecule possesses a more π-acidic character than Cl^- itself. Therefore, ligand exchange is limited to strong Lewis bases, such as phosphines[2] or arsines.[3] No reaction takes place between $[OsCl_6]^{2-}$ and weaker donor molecules such as alcohols. One approach to introduce the latter type of donors in Os(IV) coordination chemistry is to use $[OsCl_5(H_2O)]^-$ as the starting material. To date, however, the latter complex ion has only been generated in situ in chloride-containing aqueous solutions.[4−6] The characterization of this complex was restricted to UV−vis studies. The same holds true for $H[OsCl_5(H_2O)]\cdot$TBP, a complex that is formed by TBP extraction of $[OsCl_5(H_2O)]^-$ from chloride-containing sulfuric acid solutions.[7] However, this complex could not be isolated.

In this paper, the synthesis, isolation, structure, and bonding, as well as preliminary studies of H_2O exchange reactions, of $[OsCl_5(H_2O)]^-$ are described. The mononuclear and homobimetallic species $[AsPh_4][OsCl_5L]\cdot x$EtOH [L = H_2O, $x = 2$; L = EtOH, $x = 1$] and $[AsPh_4]_2[Cl_5Os(pyz)OsCl_5]$ are the first examples of osmium(IV) coordination chemistry.

Experimental Section

UV−vis spectra were recorded on a Perkin-Elmer Lambda 40 spectrophotometer. IR spectra were recorded on a Bruker IFS 48 spectrometer as CsI pellets. The Raman spectra were recorded using a Dilor LabRam spectrometer. Melting (decomposition) points were determined with a Gallenkamp MFB 595 010 M melting point apparatus. The UV−vis spectra were recorded on a Perkin-Elmer Lambda 40 spectrometer. Electrochemical measurements were performed by cyclic voltammetry in solutions of $[N^nBu_4]PF_6$ (0.1 mol dm^{-3}) in CH_2Cl_2 at 290 and 260 K, using a standard three-electrode Pt−Pt-calomel cell and a Radiometer DEA 101 potentiostat. A scan rate of 100 mV s^{-1} was used. All potentials were referenced to the ferrocene/ferrocenium couple ($E_{1/2} = 0.000$ V). Commercial OsO_4, $P(O)(O^nBu)_3$, $[P^nBu_4]Cl$, $[AsPh_4]Cl$, pyridine (py), and pyrazine (pyz) were used without further purification. C_2H_5OH was distilled from sodium hydroxide before use. CH_2Cl_2 was distilled from CaH_2. Microanalyses were performed by the Laboratory of Elemental Analysis of the Technische Universität Bergakademie Freiberg and the Laboratory of Organic Microanalysis, Nesmeyanov Institute of Organometallic Compounds (Moscow).

Synthesis of $[AsPh_4][OsCl_5(H_2O)]\cdot 2EtOH$ (9). OsO_4 (**1**) (1.0 g, 3.93 mmol) dissolved in 25 mL of a 0.2 M KOH aqueous solution was added at 25 °C to a solution of 3.0 M H_2SO_4 (1.0 L) containing NaCl (58.5 g, 1.0 mol) and Na_2SO_3 (12.6 g, 0.1 mol). The reaction mixture was heated to 100 °C for 30 min. After the reaction mixture was cooled to 25 °C, the obtained product mixture containing $[OsCl_5(H_2O)]^-$ (**2**), $[OsCl_6]^{2-}$ (**3**), and $[\{OsCl_3(OH)(H_2O)\}_2(\mu\text{-}OH)]^-$ (**4**) was extracted 10 times with 200 mL of 50 vol % of TBP (**5**) in decane (TBP/H_2O ratio = 1:5; TBP = tributyl phosphate, $P(O)(O^nBu)_3$). The combined extracts were washed 6 times with 0.1 M H_2SO_4 (TBP/H_2O ratio = 20:1). The aqueous and organic phases were separated after each washing. Addition of $[P^nBu_4]Cl$ (**6**) (0.80 g, 2.70 mmol) to the aqueous phase from the first six washes (Scheme 1) induces the selective precipitation of $[P^nBu_4]_2[OsCl_6]$ (**7**). The complex ions **2** and **4** remain in solution. Yield of **7**: 0.10 g (0.11 mmol, 3% based on OsO_4). The organic phase, which still contained some $[OsCl_5(H_2O)]^-$, was further washed 10 times with 0.1 M H_2SO_4 (TBP/H_2O ratio = 10:1). Addition of $[AsPh_4]Cl$ (**8**) (2.40 g, 5.26 mmol) to the combined aqueous phases from this wash caused the precipitation

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(1) Griffith, W. P. *Osmium, Comprehensive Coordination Chemistry*; G. Wilkinson, Ed.; Pergamon Press: Oxford, 1987; Vol. 4, p 613.
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(5) Miano, R. R.; Gardner, C. S. *Inorg. Chem.* **1965**, *4*, 337.
(6) Müller, H.; Scheible, H.; Martin, S. *Z. Anorg. Allg. Chem.* **1980**, *462*, 18.
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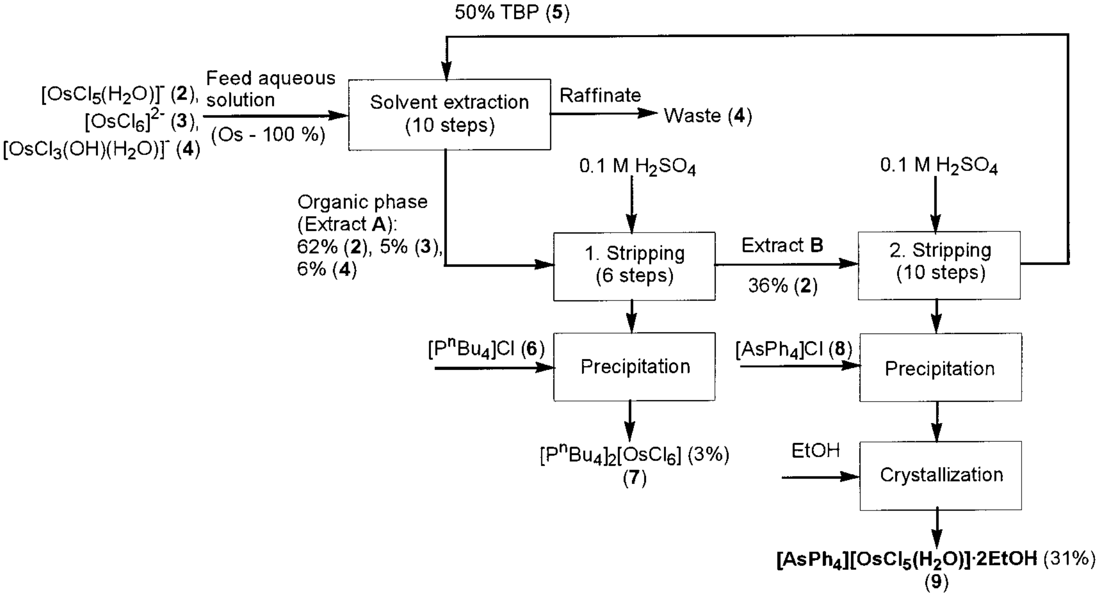
10.1021/ic000084c CCC: $19.00

Scheme 1. Flow Sheet for the Isolation of **2** and **3** as **7** and **9** from **4**



of $[AsPh_4][OsCl_5(H_2O)]$. The product was recrystallized from CH_2Cl_2/EtOH solution (1:1, v/v) at 25 °C to give crystals of $[AsPh_4][OsCl_5(H_2O)]\cdot 2EtOH$ (**9**) suitable for X-ray structure analysis. Yield: 1.05 g (1.22 mmol, 31% based on OsO_4).

Mp: 237 °C (dec). IR(Os−Cl): 309 cm^{-1}, (Os−O) 467 cm^{-1}. Raman (Os−Cl): 336 cm^{-1}, (Os−O) 444 cm^{-1}. UV−vis (CH_2Cl_2): $\lambda_{max} = 351$ nm ($\epsilon = 7.2 \times 10^3$ L cm^{-1} mol^{-1}). Potential of Os(IV)/Os(III) redox couple: $E_{1/2} = -0.70$ V ($\Delta E = 140$ mV, $T = 260$ K). Anal. Calcd for $C_{28}H_{34}AsCl_5O_3Os$: C, 39.06; H, 3.99. Found: C, 39.81; H, 3.54.

Synthesis of $[AsPh_4][OsCl_5L]\cdot xEtOH$ [L = EtOH, $x = 1$ (10a); L = py, $x = 0$ (10b)]. $[AsPh_4][OsCl_5(H_2O)]\cdot 2EtOH$ (**9**) (0.23 g, 0.26 mmol) was dissolved in 5 mL of CH_2Cl_2. A total of 50 mL of C_2H_5OH (synthesis of **10a**) or 0.21 g of py (py = pyridine) in 50 mL of CH_2Cl_2 (synthesis of **10b**) was added, and the reaction mixture was heated to reflux for 30 min. After the mixture was cooled to 25 °C, volatiles were removed in vacuo to afford $[AsPh_4][OsCl_5L]\cdot xEtOH$ [L = EtOH, $x = 1$ (**10a**), reaction of **9** with C_2H_5OH; L = py, $x = 0$ (**10b**), reaction of **9** with py] as brown solids.

Yield of **10a**: 0.22 g (0.26 mmol, 100% based on **9**). Single crystals of **10a** for X-ray structure analysis were obtained by crystallization from EtOH at 25 °C. Mp: 245 °C (dec). IR(Os−Cl) 316 cm^{-1}, (Os−O) 469 cm^{-1}. Raman (Os−Cl) 349 cm^{-1}. UV−vis (CH_2Cl_2): $\lambda_{max} = 353$ nm ($\epsilon = 7.0 \times 10^3$ L cm^{-1} mol^{-1}). Potential of Os(IV)/Os(III) redox couple: $E_{1/2} = -0.75$ V ($\Delta E = 110$ mV). Anal. Calcd for $C_{28}H_{32}AsCl_5O_5Os$: C, 41.47; H, 3.99. Found: C, 39.78; H, 3.19.

Yield of **10b**: 0.21 g (0.26 mmol, 100% based on **8**). The spectroscopic data of **10b** are summarized in ref 8.

Synthesis of $[AsPh_4]_2[Cl_5Os(pyz)OsCl_5]$ (12). $[AsPh_4][OsCl_5(H_2O)]\cdot 2EtOH$ (**9**) (0.33 g, 0.39 mmol) was dissolved in 40 mL of CH_2Cl_2, and 15 mg (0.19 mmol) of pyz (pyz = pyrazine) (**11**) was added. The reaction mixture was heated to reflux for 1 h. The solution was concentrated to ca. 3 mL and passed through a pad of silica gel (CH_2Cl_2 eluent). The first dark fraction was isolated. After removal of solvent in vacuo a dark-brown solid was obtained. Yield: 0.26 g, 0.17 mmol (85%).

Mp: 265 °C (dec). IR(Os−Cl): 307 cm^{-1}. UV−vis (CH_2Cl_2): $\lambda_{max} = 378$ nm ($\epsilon = 1.53 \times 10^4$ L cm^{-1} mol^{-1}). Potentials of the Os(IV)/Os(III) redox couples: $E^1_{1/2} = -0.28$ V ($\Delta E = 100$ mV), $E^2_{1/2} = -0.59$ V ($\Delta E = 80$ mV). Anal. Calcd for $C_{52}H_{44}N_2As_2Cl_{10}O_5Os$: C, 39.49; H, 2.80. Found: C, 40.13; H, 3.18.

Structure Determination and Refinement of Complexes 9 and 10a. X-ray structure data (total/unique reflections: **9**, 5076/9843; **10a**, 5636/8353) were collected at 170 K on a Bruker SMART CCD diffractometer for yellow (**9**) and brown (**10a**) crystals. Each crystal was attached to a glass fiber with perfluorinated polyether. The unit cell parameters were checked for the presence of higher lattice symmetry.[8] Data were corrected for absorption using SADABS.[10] The structures were solved by direct methods (SHELX-97).[11] Refinement was carried out by full matrix least-squares techniques on F^2 (SHELXL-97/2).[11] Hydrogen atoms were located from the difference Fourier map. All hydrogens except H(101), H(201), and H(102) for **9** and H(101) and H(201) for **10a**, which were fully refined, were included on their ideal positions, riding on their carrier atoms. All non-hydrogen atoms were refined anisotropically. Crystal data and numerical details of the structure determination and refinement are listed in Table 1. Selected geometrical details for **9** and **10a** are listed in Table 2.

Table 1. Experimental Data for the X-ray Diffraction Studies of Complexes **9** and **10a**

	9	10a
formula	$C_{28}H_{34}AsCl_5O_3Os$	$C_{28}H_{32}AsCl_5O_2Os$
fw	860.92	842.91
space group	monoclinic	monoclinic
cryst syst	$P2_1/n$	$P2_1/n$
Z	4	4
a (Å)	10.910(4)	10.7762(2)
b (Å)	17.127(5)	17.3939(1)
c (Å)	17.555(7)	17.1477(3)
β (deg)	103.77(2)	103.645(1)
V (Å^3)	3186(2)	3123.45(8)
d_{calc} (g cm^{-3})	1.795	1.792
μ(Mo Kα) (mm^{-1})	5.481	5.586
radiation (Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp (K)	173(2)	173(2)
R^a ($I > 2\sigma(I)$)/all	0.0704/0.1572	0.0417/0.0843
R_w/wR2 ($I > \sigma(I)$)/all	0.1084/0.1331	0.0729/0.0856
max/min transm	0.8622/0.6985	0.5289/0.3013
completeness all data	53.5	87.1

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$.

Results

The pentachloroaquoosmate(IV) $[OsCl_5(H_2O)]^-$ (**2**) was obtained in 63% yield when OsO_4 (**1**) in a 0.2 M KOH solution

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(8) Skukla, A. K.; Zerbe, H. Z.; Preetz, W. *Z. Anorg. Allg. Chem.* **1980**, *468*, 39.

(9) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

(10) *Area-Detector Absorption Corrections*; Siemens Industrial Automation, Inc.: Madison, WI, 1996.

(11) Sheldrick, G. M. *SHELX-97, Programs for Crystal Structure Analysis*, release 97-2; University of Göttingen: Göttingen, Germany, 1997.

Table 2. Selected Geometrical Details of Complexes **9** and **10a**[a]

	9	**10a**
	Bond Distances [Å]	
Os1−Cl1	2.352(3)	2.3518(13)
Os1−Cl2	2.280(4)	2.2895(13)
Os1−Cl3	2.328(3)	2.3282(13)
Os1−Cl4	2.305(4)	2.3184(13)
Os1−Cl5	2.332(5)	2.3233(13)
Os1−O1	2.030(17)	2.080(4)
O1−H101	0.79(7)	0.86(5)
O1−H201	0.83(12)	
O1−H102	1.3(3)	
O1−C1		1.500(6)
O1−O2	2.240(3)	2.567(5)
O1−O3	2.530(3)	
O3−H101		
O2−H101		1.75(6)
O1−H102	1.3(3)	
	Bond Angles [deg]	
Cl2−Os1−O	179.1(8)	178.18(13)
Os1−O1−H101	105(10)	111(4)
Os1−O1−H201	112(10)	
H101−O1−H201	118(10)	
Os1−O1−C1		127.9
O1−H101−O3	146.21	
O1−H101−O2		158.5

[a] The estimated standard deviations of the last significant digits are shown in parentheses.

is treated with a 3.0 M H_2SO_4 solution containing 1.0 M NaCl and 0.1 M Na_2SO_3 and heated to 100 °C for 30 min (eq 1). The

$$\underset{\mathbf{1}}{OsO_4} \xrightarrow[3\ M\ H_2SO_4,\ \Delta T]{Na_2SO_3,\ NaCl} \boxed{\underset{\mathbf{2}}{[OsCl_5(H_2O)]^-}} + \underset{\mathbf{3}}{[OsCl_6]^{2-}} + \underset{\mathbf{4}}{[\{OsCl_3(OH)(H_2O)\}_2(\mu\text{-}OH)]^-} \qquad (1)$$

course of the reaction was followed by UV−vis spectroscopy, where formation of $[OsCl_5(H_2O)]^-$ is indicated by an increase in the intensity of a characteristic absorption band at 345 nm.[6]

The complex ion $[OsCl_5(H_2O)]^-$ (**2**), formed by the reduction of **1** with Na_2SO_3 in a chloride-containing sulfuric acid solution, was separated by solvent extraction with 50 vol % of $P(O)(O^nBu)_3$ (**5**) in decane [$P(O)(O^nBu_4)_3$ = TBP], as outlined in Scheme 1.

Though the extraction of $[OsCl_6]^{2-}$ (**3**) with organophosphorus compounds is a well-established method,[12] this procedure has not been used to recover $[OsCl_5(H_2O)]^-$ (**2**) from aqueous solutions so far. For our study we choose TBP, which is an efficient extractant with good Lewis basicity.[13] It was found that **2** could be extracted from chloride-containing sulfuric acid solutions as $H[OsCl_5(H_2O)]\cdot TBP$ solvate.[7] The distribution coefficient of osmium

$$D = \frac{[Os]_{org}}{[Os]_{aq}}$$

in this extraction is 14.8, and the equilibrium concentration of **2** in the aqueous phase is $[Os]_{aq} = 5.6 \times 10^{-4}$ mol/L. The distribution coefficients of complexes **2** and **3** at various stages of extraction process are as follows: extraction $D_2 = 14.8$, $D_3 = 22.2$; first stripping, $D_2 = 0.20$, $D_3 = 0.11$; second stripping, $D_2 = 0.46$.

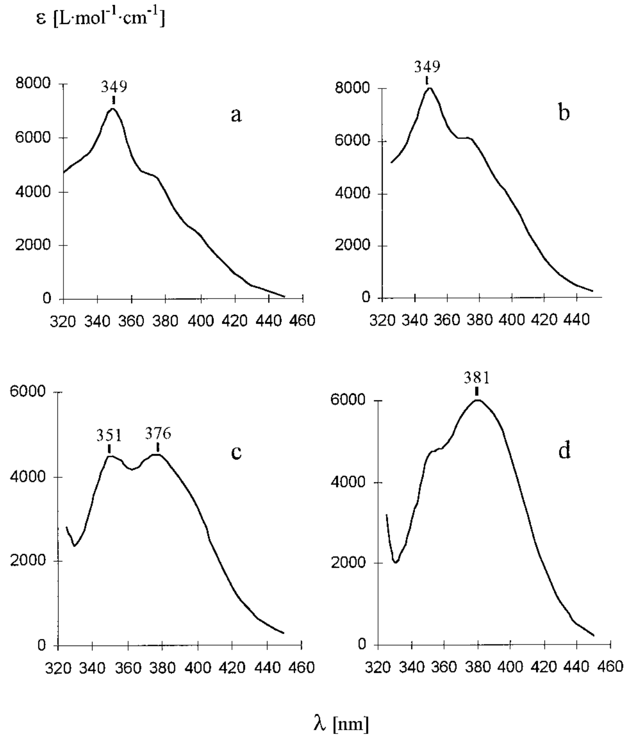

Figure 1. Selected UV−vis spectra of the organic extracts of the first (a), fifth (b), sixth (c), and seventh (d) steps.

To obtain the highest concentration of osmium in the organic phase, a 10-step countercurrent process was used (extraction, Scheme 1). UV−vis spectroscopic studies show that in addition to **2**, another osmium complex (**4**) with an absorption maximum at 378 nm was formed in the aqueous phase and was partly extracted with TBP. Müller et al. previously reported the synthesis of $[\{OsCl_3(OH)(H_2O)\}_2(\mu\text{-}OH)]^-$ (**4**), which has a characteristic absorption band at 378 nm.[6] This complex shows an absorption maximum at 381 nm in the organic phase, due to a decrease of solvent polarity (Figure 1). UV−vis spectra measured for all of the 10 extracts clearly show that **2** is almost completely extracted in the first six steps (Figure 1).

In the last four steps (out of 10), the extraction of **4** prevails. Nevertheless, the majority of the homodinuclear complex ion **4** remains in the aqueous phase because of the relatively small distribution coefficient of **4** ($D_4 = 0.4$).

After the extraction with TBP, the organic phase (extract A, Scheme 1) contains the complex ions **2**, **3**, and **4**. Therefore, it was necessary to strip the last two osmium complexes with a 0.1 M solution of H_2SO_4 to further isolate $[OsCl_5(H_2O)]^-$ (**2**). The use of dilute H_2SO_4 prevents hydrolysis of the corresponding chloroosmium complexes (vide supra), which takes place when water is used as a stripping agent. The first six steps of the stripping process remove the complex ion **3** and the remainder of **4** from the organic extract A (Scheme 1). Complex ion **2** also goes partially into aqueous phase during the first stripping. Addition of $[P^nBu_4]Cl$ (**6**) as a 0.1 M solution to the corresponding stripping solution precipitates only $[P^nBu_4]_2[OsCl_6]$ (**7**) in an overall yield of 3%. After the precipitation of **7**, the complex ions **2** and **4** remain in the aqueous solution, which can be attributed to their single negative charges, resulting in increased solubility of the corresponding phosphonium salts. Further stripping of ion **2** from extract B (Scheme 1) was achieved with a 0.1 M solution of H_2SO_4. $[OsCl_5(H_2O)]^-$ (**2**) was converted to $[AsPh_4][OsCl_5(H_2O)]$ by addition of $[AsPh_4]Cl$ (**8**) to the aqueous solution of the second 10-step stripping

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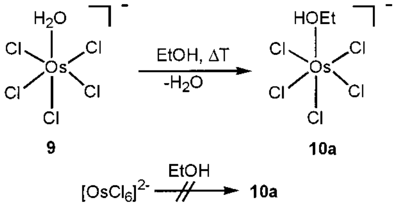
(12) Meier, H.; Zimmerhackl, E.; Albrecht, W.; Bösche, D.; Hecker, W.; Menge, P.; Ruckdeschel, A.; Unger, E. *Microchim. Acta* **1969**, *3*, 573.

(13) Cox, M.; Douglas, S. F. Metal Extraction Chemistry. In *Handbook of Solvent Extraction*; Lo, T. C., Baird, M. H. I., Hanson, C., Eds.; Krieger: Malabar, 1991; p 68.

process (Scheme 1). After crystallization from a dichloromethane/ethanol solution, $[AsPh_4][OsCl_5(H_2O)]\cdot 2EtOH$ (**9**) was obtained as brownish crystalline material in an overall yield of 31%. This complex is stable in air for extended periods of time and is readily soluble in polar organic solvents such as dichloromethane, chloroform, and acetone.

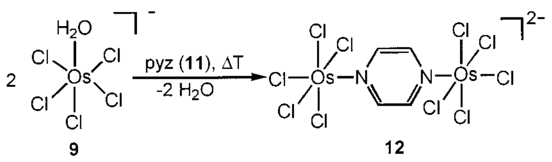
A weakly bonded H_2O ligand is present in **9**. Therefore, this complex is suitable for ligand exchange reactions. One example is given in eq 2, where EtOH was added to a dichloromethane solution of **9**. This mixture was refluxed for 30 min, and after



(2)

appropriate workup, complex $[AsPh_4][OsCl_5(EtOH)]\cdot EtOH$ (**10a**) was isolated as a deep-brown solid in quantitative yield (eq 2). Also, pyridine (py) can be applied as a Lewis base in the reaction with **9** to produce the complex $[AsPh_4][OsCl_5(py)]$ (**10b**) in quantitative yield.

Treatment of **9** with pyrazine (**11**) in a 2:1 molar ratio (eq 3) in dichlormethane as solvent affords the homobinuclear osmium (IV) complex $[AsPh_4]_2[Cl_5Os(pyz)OsCl_5]$ (**12**), after appropriate workup, in 85% yield as a dark-brown solid. In complex **12**,



(3)

two identical $OsCl_5^-$ units are bridged by the π-conjugated organic group pyz through Os−N dative bonds.

Structures of 9 and 10a in the Solid State. The molecular structures of $[AsPh_4][OsCl_5(H_2O)]\cdot 2EtOH$ (**9**) and $[AsPh_4][OsCl_5(EtOH)]\cdot EtOH$ (**10a**) were determined by X-ray diffraction. Experimental crystal data are listed in Table 1, and geometric details are listed in Table 2.

Both complexes crystallize in the monoclinic space group $P2_1/n$ with two molecules of EtOH (**9**) or one molecule of EtOH (**10a**), which form stable solvates with the corresponding transition metal complex anions via hydrogen bridges. The metal center Os1 possesses, as expected, a pseudo-octahedral environment consisting of the five chloro ligands Cl(1)−Cl(5) and the H_2O molecule (**9**) or the EtOH (**10a**) group. The osmium−chlorine bond lengths for both compounds are in the range 2.305−2.353 Å for the Os(1)−Cl(1,3−5) interatomic bond distances (Table 2). These values are typical for Os−Cl bonds, such as those experimentally observed for $[OsCl_6]^{2-}$ (2.332−2.335 Å).[14] In contrast to this finding the Os(1)−Cl(2) distances of 2.280(4) Å for **9** and 2.2895(13) Å for **10a** are shorter than the other ones, which can be explained by the trans influence of the datively bound H_2O (**9**) or EtOH (**10a**) groups.

The aquo ligand present in $[OsCl_5(H_2O)]^-$ gives rise to the formation of the solvate adduct $[AsPh_4][OsCl_5(H_2O)]\cdot 2EtOH$ (**9**). Hydrogen bridges between the oxygen atoms of H_2O and EtOH are found [H(101)−O(3), 1.8(2) Å; H(102)−O(1), 1.3(3) Å] (Table 2). The distances O(1)−O(2) and O(1)−O(3) are 2.240(3) and 2.530(3) Å, which clearly meets the criterion for the existence of hydrogen bridges (expected: <2.7 Å).[15]

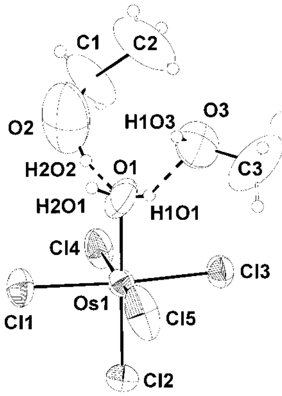


Figure 2. ORTEP drawing (drawn at 50% probability level) of complex **9** (cation is omitted for clarity).

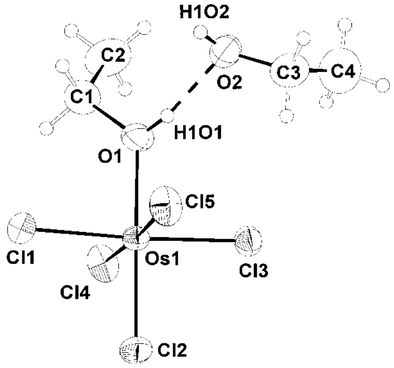


Figure 3. ORTEP drawing (drawn at 50% probability level) of complex **10a** (cation is omitted for clarity).

As with the aquo ligand in **9**, the coordinated EtOH group in **10a** gives rise to the association of a second EtOH molecule via a hydrogen bridge, which is formed between O(1) and O(2) (Figure 3). The distance O(1)−O(2) is 2.567(5) Å, which again is in accordance with the above-mentioned criterion for hydrogen bridges between oxygen atoms.[15]

In the structures of molecules containing either $[PPh_4]^+$ or $[AsPh_4]^+$ as counterion, two packing modes are observed. For the cation/anion ratio of 1:1, columnlike structures are usually observed,[16] while for the ratio of 2:1 pairs of $([EPh_4]^+)_2$ cations (E = P, As) are favored.[16] However, in the case of **9** and **10a** in which the cation-to-anion ratio is 1:1, neither of these structures could be observed. The $[AsPh_4]^+$ ions in these species are independent and noncoordinating counterions.

Spectroscopic Studies. Complexes **9**, **10**, and **12** were characterized by UV−vis, IR, and Raman spectroscopy.

In the UV−vis spectra of aqueous solutions containing $[OsCl_5(H_2O)]^-$ (**2**), one distinct absorption band is observed at λ_{max} = 345 nm ($\epsilon = 7.1 \times 10^3$ L cm^{-1} mol^{-1}), while dichloromethane solutions of **9** absorbed at λ_{max} = 351 nm with $\epsilon = 7.2 \times 10^3$ L cm^{-1} mol^{-1}. The UV−vis spectrum of **10a** is very similar to that of **9**, with one band at λ_{max} = 353 nm ($\epsilon = 7.0 \times 10^3$ L cm^{-1} mol^{-1}). The UV−vis spectra of both complexes can be used for a rapid characterization of these species, since they are quite distinct from the spectra of $[OsCl_6]^{2-}$ (**2**) and $[\{OsCl_3(OH)(H_2O)\}_2(\mu\text{-}OH)]^-$ (**4**).[6] The UV−vis spectrum of **12** shows one absorption band at 378 nm ($\epsilon = 1.53 \times 10^4$ L cm^{-1} mol^{-1}).

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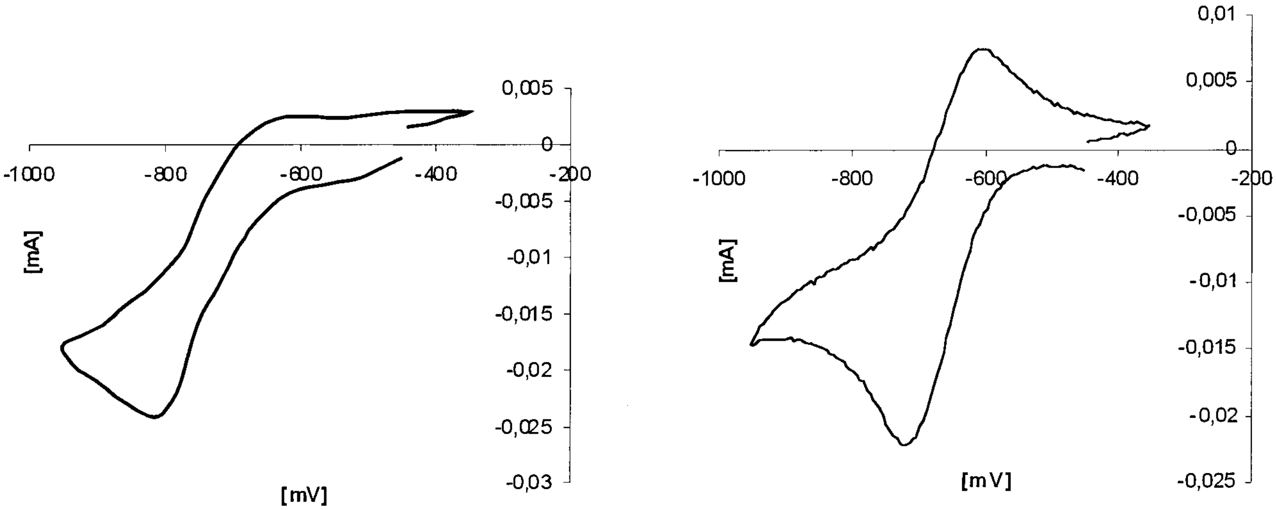

Figure 4. Cyclic voltammograms of $[AsPh_4][OsCl_5(H_2O)]{\cdot}2EtOH$ (**9**) at 290 K (left) and 260 K (right).

IR and Raman spectroscopy was used to characterize **9** and **10a**. As expected for chloro complexes of platinum metals,[18] a broad band for the Os−Cl stretching frequencies is found at 316 cm^{-1} for **10a**, 309 cm^{-1} for **9**, and 307 cm^{-1} for **12** in the IR spectrum. The difference in the frequency for ν_{Os-Cl} is the result of the decrease of π-donating properties of ligands in the order EtOH > H_2O > pyz. Additionally, Os−Cl vibrations are observed in the Raman spectra of **9** and **10a** at 336 cm^{-1} (**9**) and 349 cm^{-1} (**10a**). The absorption bands at 467 cm^{-1} (**9**) and 469 cm^{-1} (**10a**) in the IR spectra can be attributed to the ν_{Os-O} stretching vibrations.[19] The ν_{Os-O} stretching vibration is also observable in the Raman spectrum of **9** at 444 cm^{-1}; however, this band cannot be detected for complex **10a**.

Electrochemical Studies. Complex $[AsPh_4][OsCl_5L]{\cdot}xEtOH$ [L = H_2O, $x = 2$ (**9**); L = EtOH, $x = 1$ (**10a**)], $[P^nBu_4]_2[OsCl_6]$ (**7**), and $[AsPh_4]_2[Cl_5Os(pyz)OsCl_5]$ (**12**) were studied by cyclic voltammetry. It was found that the redox behavior of **9** is temperature-dependent (Figure 4). At 290 K the one-electron reduction is irreversible, while at 260 K the Os(IV)/Os(III) reduction exhibits a reversible behavior at $E_{1/2} = -0.70$ V with $\Delta E = 140$ mV. Similar observations were made for $[N^nBu_4]_2[OsCl_6]$.[20] In contrast, complex **10a** showed a reversible one-electron reduction for the Os(IV)/Os(III) redox couple ($E_{1/2} = -0.75$ V, $\Delta E = 110$ mV) at 290 K.

The potentials for the Os(IV)/Os(III) couple in **7**, **10a**, and **9** shift to more positive values as the π-donating Cl^- ligand is replaced by an EtOH or H_2O group [**7**, $E_{1/2} = -1.17$ V, $\Delta E = 130$ mV ($T = 290$ K); **10a**, $E_{1/2} = -0.75$ V, $\Delta E = 110$ mV ($T = 290$ K); **9**, $E_{1/2} = -0.70$ V, $\Delta E = 140$ mV ($T = 260$ K)]. The difference in the redox potentials for **9** and **10a** is attributed to the H_2O and EtOH ligands. EtOH is a stronger electron-donating group than H_2O, leading to a shift of the Os(IV)/Os(III) redox couple to a more negative value.

The cyclic voltammogram of **12** (Figure 5) shows two reversible one-electron reduction processes at $E^1_{1/2} = -0.28$ V and $E^2_{1/2} = -0.59$ V. The formation of the intermediate $[Cl_5Os(pyz)OsCl_5]^{3-}$ ion can be considered as the first step of the reduction process. This anion is formally a Os(IV)−Os(III) complex with the Os centers bridged through the π-conjugated organic pyrazine molecule, which has good properties for intramolecular electron-transfer studies. As expected, further reduction of this mixed-valence compound takes place at more negative potential and results in the formation of the Os(III)−Os(III) complex $[Cl_5Os(pyz)OsCl_5]^{4-}$.

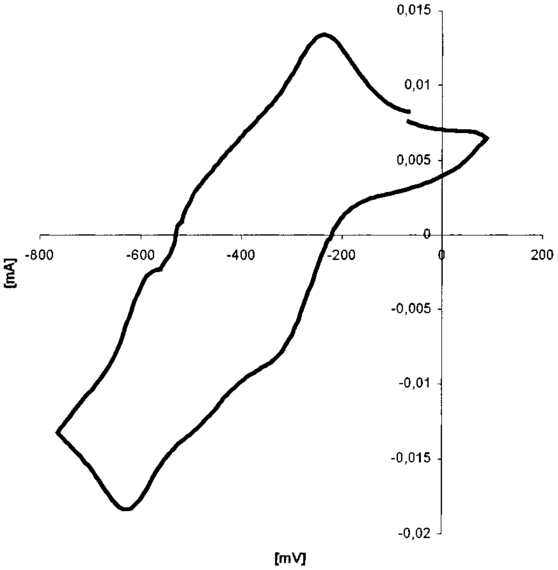

Figure 5. Cyclic voltammogram of $[AsPh_4][Cl_5Os(pyz)OsCl_5]$ (**12**) at 290 K.

Discussion

The osmium(IV) complex $[OsCl_5(H_2O)]^-$ (**2**) can easily be prepared from OsO_4 (**1**) by reaction with NaCl in sulfuric acid using Na_2SO_3 as the reducing agent. The product is isolated by solvent extraction with TBP. $[AsPh_4][OsCl_5(H_2O)]{\cdot}2EtOH$ (**9**) is the first isolated and characterized chloroaquo complex of osmium(IV). This complex can be used as an effective starting material for the synthesis of new pentachloroosmate(IV) species containing only weakly bound π-donating ligands. Thus, the reaction of **9** with two-electron donors L afforded $[AsPh_4][OsCl_5L]{\cdot}xEtOH$ [L = EtOH, $x = 1$ (**10a**); L = py (**10b**), $x = 0$] in quantitative yield. Similarly, the reaction of **9** with **11** produces the homobinuclear complex $[AsPh_4]_2[Cl_5Os(pyz)OsCl_5]$ (**12**).

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While the reactions of $[OsCl_6]^{2-}$ with strong π-acid ligands are usually not selective and afford a mixture of mono-, di-, tri-, etc. substituted derivatives, complex **9** reacts very smoothly and selectively with Lewis bases to produce mononuclear osmium(IV) complexes of the general type $[OsCl_5L]^-$ (L = two-electron donor ligand) or dinuclear species, such as $[AsPh_4]_2[Cl_5Os(pyz)OsCl_5]$ (**12**).

Complexes **9**, **10a**, **10b**, and **12** are stable toward air. They are highly soluble in polar organic solvents such as dichloromethane, chloroform, and acetone. The H_2O and the EtOH ligands in **9** and **10a** give rise to the formation of solvation spheres around the octahedrally coordinated osmium(IV) centers, as could be shown by X-ray structure analysis. In **9**, as a result of hydrogen bonding, two EtOH molecules are bound to the H_2O ligand, while in **10a** a second EtOH molecule is bound via a hydrogen bridge to the datively coordinated EtOH ligand.

The reaction chemistry of **9** is the topic of current studies.

Conclusions

$[AsPh_4][OsCl_5(H_2O)]\cdot 2EtOH$ (**9**) can be used as a starting material for the preparation of a large variety of different osmium(IV) complexes of the general types $[AsPh_4][OsCl_5L]$ (L = two-electron donating group) and $[AsPh_4]_2[Cl_5Os(LL)OsCl_5]$ (LL = bidentate ligand). Since **9** contains a weakly bound H_2O group, this complex is suited for the synthesis of further Os(IV) complexes, which contain weakly bonded L groups. Therefore, **9** presents a good opportunity to systematically study $[OsCl_5L]^-$ complexes.

Acknowledgment. This work was supported in part by the Volkswagenstiftung, Fonds der Chemischen Industrie and the DAAD (A.M.). We are grateful to Dr. S. Back for many fruitful discussions and to Degussa-Hüls AG for many chemicals gifts.

Supporting Information Available: Tables of crystal data and details of the structure determinations, final coordinates and equivalent isotropic parameters of non-hydrogen atoms, hydrogen atoms positions and isotropic thermal parameters, anisotropic thermal parameters, and bond distances and bond angles for **9** and **10a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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