pathway requires immediate termination of the proton-exchange process, and the present experiments do not provide detailed further constraints on the mechanistic detail. The mechanism for the rapid scrambling is similar to one that has been suggested for platinum(IV) complexes by Grunwald,[7] wherein the water solvating the cation interacts simultaneously with the proton-deficient nitrogen atom and an adjacent coordinated ammonia molecule. The very rapid exchange kinetics, implied by this earlier result, appears to be consistent with our present findings.

In summary, this series of ^{59}Co spectra shows very clearly the requirement of two different proton-exchange paths for this complex. Though this study shows the power of ^{59}Co NMR to elucidate mechanistic details of proton-exchange processes, it falls far short of the potential development in this area because it lies beyond the primary interest of the laboratory.

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Registry No. Hexaamminecobalt(III), 14695-95-5; water, 7732-18-5; triethylamine, 121-44-8.

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Redox Chemistry of Multiply Bonded Diosmium Complexes: Preparation and Characterization of Complexes Containing Osmium–Osmium Bonds of Order 2.5

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The complexes $Os_2(O_2CR)_4Cl_2$ (R = C_2H_5 or C_3H_7) and $Os_2(hp)_4Cl_2$ (hp is the monoanion of 2-hydroxypyridine) each possess a reversible one-electron reduction at $E_{1/2} \simeq +0.3$ V (for the carboxylates) or +0.1 V (for the hp derivative) vs. SCE. These reductions can be accomplished chemically by using cobaltocene as the reducing agent to produce $[(\eta\text{-}C_5H_5)_2Co][Os_2(O_2CR)_4Cl_2]$ and $[(\eta\text{-}C_5H_5)_2Co][Os_2(hp)_4Cl_2]$. These complexes are the first derivatives of the Os_2^{5+} core to have been isolated and have been characterized by cyclic voltammetry, electronic absorption spectroscopy, ESR spectroscopy, and magnetic susceptibility measurements. They are believed to contain Os–Os multiple bonds of order 2.5 with the configurations $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*2}$ ($S = {}^3/_2$) and $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*1}$ and/or $\sigma^2\pi^4\delta^2\pi^{*3}$ ($S = {}^1/_2$) being the principal contributors to the ground state at room temperature.

Introduction

Recently, various strategies have been explored for the synthesis of diosmium carboxylates, especially with a view to the isolation of compounds that might contain osmium–osmium multiple bonds. One such approach involved the use of the complexes *trans*-$OsO_2X_2(PR'_3)_2$ as synthetic starting materials,[2] and this led to the isolation and structural characterization of the novel, diamagnetic diosmium(IV) species $Os_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2X_4(PR'_3)_2$.[3,4] Among the properties of note for this class of complexes (R = CH_3 or C_2H_5; X = Cl or Br; PR'_3 = PPh_3 or PEt_2Ph) is the occurrence of a very accessible one-electron reduction ($E_{1/2}$ values in the range +0.09 to +0.23 V vs. SCE) to give the paramagnetic $Os^{III}Os^{IV}$ monoanions.[4] On the other hand, when recourse was made to a different osmium starting material, namely, the hexachloroosmate(IV) ion, then reaction with acetic acid–acetic anhydride was found to give the diosmium(III) acetate $Os_2(O_2CCH_3)_4Cl_2$.[5] Subsequently, other diosmium(III) carboxylates $Os_2(O_2CR)_4Cl_2$ (R = Et, *n*-Pr, or CH_2Cl) were discovered[6,7] and the crystal structures of the acetate, propionate and butyrate were determined,[6-8] thereby establishing that these complexes are derivatives of the multiply bonded Os_2^{6+} core.[9]

We have explored the redox chemistry of these diosmium(III) complexes with a view to understanding their relationship to the well-established class of diruthenium carboxylates[10] and various derivatives that contain the isoelectronic triply bonded Re_2^{4+} core.[11,12] We provide in this report details of the redox chemistry of these diosmium(III) species which establish quite clearly that they undergo a facile one-electron reduction to give compounds that contain the hitherto unknown Os_2^{5+} core.

Experimental Section

Materials. All solvents were dried over molecular sieves, distilled, and purged with nitrogen gas for 30 min prior to use. Cobaltocene was purchased from Strem Chemicals, Inc., and was used as received. The *n*-propionate and *n*-butyrate complexes of the type $Os_2(O_2CR)_4Cl_2$ were prepared from $[OsCl_6]^{2-}$ solutions by using the procedure described previously.[7]

Reaction Procedures. All syntheses were carried out under an atmosphere of nitrogen.

$Os_2(hp)_4Cl_2 \cdot 2H_2O$. This complex, where Hhp = 2-hydroxypyridine, was prepared by a modification of the existing procedure.[7] A mixture of $Os_2(O_2CC_3H_7)_4Cl_2$ (112.7 mg, 0.141 mmol) and Hhp (116.7 mg, 1.23 mmol) was refluxed in 10 mL of ethanol for 45 min. The deep red solution was cooled to room temperature, and the solvent was removed by evaporation in an N_2 stream. Dichloromethane was then added to dissolve the dark red residue, and this solution was filtered through a medium-porosity frit. The volume of this solution was reduced to approximately 5 mL, and 5 mL of diethyl ether was added to initiate precipitation of the product. This mixture was refrigerated

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overnight to afford a high yield of the dark red product $Os_2(hp)_4Cl_2{\cdot}2H_2O$; yield 102.5 mg (84%). Anal. Calcd for $C_{20}H_{20}Cl_2N_4O_6Os_2$: C, 27.81; H, 2.34. Found: C, 28.10; H, 2.62. The presence of water in the complex was confirmed by ^1H NMR spectroscopy. Note that the present procedure utilizes $Os_2(O_2CC_3H_7)_4Cl_2$ rather than $Os_2(O_2CCH_3)_4Cl_2$,[7] a modification that results in an appreciable increase in the product yield (from 51% to 84%).

In our hands, recrystallized samples of this complex could be obtained as a wide variety of solvates. ^1H NMR spectroscopy of various samples showed the presence of small amounts of lattice ethanol, diethyl ether, or dichloromethane, in addition to water. Indeed, Cotton and Thompson,[13] who first prepared and structurally characterized this complex, had commented previously upon its propensity to form solvates.

$[(\eta\text{-}C_5H_5)_2Co][Os_2(O_2CC_3H_7)_4Cl_2]$. A quantity of $Os_2(O_2CC_3H_7)_4Cl_2$ (83.1 mg, 0.104 mmol) was added to 10 mL of acetone and the resulting solution treated with a close to stoichiometric amount of cobaltocene (23.2 mg, 0.123 mmol). The reaction mixture was then stirred at room temperature for 30 min, and the yellow-green precipitate that had formed was filtered off, washed with several portions of acetone and diethyl ether, and then dried; yield 86.4 mg (84%). Anal. Calcd for $C_{26}H_{38}Cl_2CoO_8Os_2$: C, 31.58, H, 3.88. Found: C, 31.70; H, 3.95.

$[(\eta\text{-}C_5H_5)_2Co][Os_2(O_2CC_2H_5)_4Cl_2]$. This complex was prepared by using a procedure analogous to that described for the butyrate; yield 82%. Anal. Calcd for $C_{22}H_{30}Cl_2CoO_8Os_2$: C, 28.33; H, 3.25. Found: C, 28.07; H, 3.28.

$[(\eta\text{-}C_5H_5)_2Co][Os_2(hp)_4Cl_2]$. Cobaltocene (30.1 mg, 0.159 mmol) was placed in a three-necked round-bottomed flask fitted with a rubber septum, an inlet for the influx of nitrogen gas or application of a vacuum, and a filter frit. After this system was purged with dinitrogen, a 10-mL solution of $Os_2(hp)_4Cl_2$ (115.1 mg, 0.139 mmol) in dichloromethane was added via a cannula. Within 15 min, the color of this solution had changed from dark red to olive green. After 30 min, 15 mL of deoxygenated diethyl ether was added to induce precipitation of the product, $[(\eta\text{-}C_5H_5)_2Co][Os_2(hp)_4Cl_2]$. The reaction mixture was filtered under dinitrogen to remove the olive green solid, which was washed several times with diethyl ether and then was vacuum-dried for 20 min; yield 103.6 mg (73%). Anal. Calcd for $C_{30}H_{26}Cl_2CoN_4O_4Os_2$: C, 35.43; H, 2.58. Found: C, 35.34; H, 2.75. This complex is extremely air sensitive, especially in solution but also in the solid state, and must be stored and manipulated under nitrogen or argon gas at all times.

Physical Measurements. Electronic absorption spectra were obtained on dichloromethane solutions with an IBM Instruments Model 9420 (Purdue University) or Beckman Acta MIV (Edinburgh University) spectrophotometer. In the near-IR region appropriate background corrections were imposed. X-Band ESR spectra were obtained on toluene/dichloromethane glasses (5/2, v/v) at −160 °C with a Varian E-109 spectrometer. Magnetic susceptibilities were determined by the Evans method[14] on dichloromethane solutions with a Perkin-Elmer R32 (Purdue University) or Bruker WP80SY (Edinburgh University) NMR spectrometer. Routine cyclic voltammetry experiments were carried out on solutions in 0.2 M $n\text{-}Bu_4NPF_6\text{–}CH_2Cl_2$ and were performed as described previously.[15] The electrochemical generation of anions for subsequent spectroscopic characterization was carried out at 293 K by controlled-potential electrolysis at 0.00 V (vs. a Ag/AgCl reference electrode) of $n\text{-}Bu_4NF\text{–}CH_2Cl_2$ solutions of the complexes in an OTTLE cell (with a Pt-gauze working electrode and Infrasil windows).[16]

Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Results and Discussion

Cyclic voltammetric measurements on 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH)–dichloromethane solutions of the propionate and butyrate complexes $Os_2(O_2CR)_4Cl_2$ show that each complex exhibits a reversible one-electron couple[17,18] at $E_{1/2} = +0.29$ and $+0.30$ V, respectively, vs. SCE (see Figure 1a). For each couple, $i_{p,a}/i_{p,c} = 1$ and $i_p/v^{1/2}$ ratios were constant in the sweep rate range 50–400 mV/s, in accord with diffusion control. At $v = 200$ mV/s, the potential separation ΔE_p between the anodic and cathodic peaks was 100 mV and increased slightly with increase in scan rate. A second couple is observed at $E_{1/2} \simeq +1.75$ V vs. SCE upon extending the scan to +2.0 V. This process corresponds to a one-electron oxidation. While electrochemical behavior similar to that described above is observed in 0.1 M TBAH–acetonitrile, the oxidation now appears to be electrochemically irreversible ($i_{p,c}/i_{p,a} < 1$) although it occurs at a very similar potential ($E_{p,a} = +1.78$ V in the case of R = *n*-Pr).

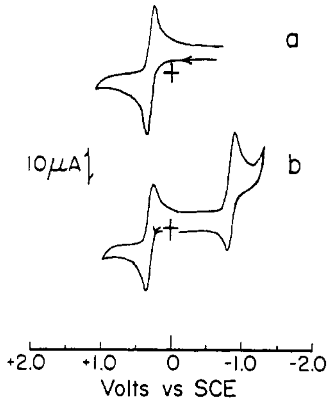

Figure 1. Cyclic voltammograms (measured at 200 mV/s in 0.2 M TBAH–CH_2Cl_2 at a Pt-bead electrode): (a) $Os_2(O_2CC_3H_7)_4Cl_2$; (b) $[(C_5H_5)_2Co][Os_2(O_2CC_3H_7)_4Cl_2]$.

The couple at $E_{1/2} \simeq +0.3$ V corresponds to a one-electron reduction.[19] Consistent with our interpretation, we find that the controlled-potential electrolysis of such solutions at +0.20 V ($n = 1.0 \pm 0.1$ by coulometry) generates solutions containing the quite stable monoanion. Attempts to do this reduction chemically by using sodium or magnesium yielded intractable products. However, cobaltocene, which has been successfully used as a reducing agent[20,21] and which has a suitable reduction potential (−0.94 V vs. SCE in acetonitrile),[22] proved to be an ideal reductant. Thus, treatment of acetone solutions of $Os_2(O_2CR)_4Cl_2$ (R = C_2H_5 or C_3H_7) with cobaltocene yielded (after 30 min) an olive green precipitate of $[(C_5H_5)_2Co][Os_2(O_2CR)_4Cl_2]$. Cyclic voltammetry on 0.2 M TBAH–CH_2Cl_2 solutions of these complexes shows two reversible one-electron couples (Figure 1b): that at +0.30 V vs. SCE corresponds to the *oxidation* of the anion, while the reduction of the cobaltocenium ion is associated with the couple at −0.90 V vs. SCE.

We find that the reaction of $Os_2(O_2CC_3H_7)_4Cl_2$ with 2-hydroxypyridine (Hhp) in refluxing ethanol yields the dark

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(17) We define reversibility in terms of a comparison with the behavior of known reversible couples such as $(C_5H_5)_2Fe/(C_5H_5)_2Fe^+$ and $Ru(bpy)_3^{2+}/Ru(bpy)_3^{3+}$. The characteristics of these latter systems obtained by using our experimental set-up and the 0.2 M TBAH–CH_2Cl_2 solvent system are described elsewhere.[18]

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(19) An earlier study[7] had led to the belief that this process actually corresponded to a one-electron oxidation, an interpretation that is now known to be incorrect; see: Behling, T.; Wilkinson, G.; Stephenson, T. A.; Tocher, D. A.; Walkinshaw, M. D. *J. Chem. Soc., Dalton Trans.* **1984**, 305. In this previous report,[7] electrode potentials were quoted vs. a Ag/AgI reference electrode whereas those here are referenced to the SCE. Exact comparison requires subtraction of 0.17 V from the data of ref 7, on the basis of the observations that, for the ferrocene/ferrocenium couple, $E_{1/2} = +0.60$ V vs. Ag/AgI and $E_{1/2} = +0.43$ V vs. the SCE in the present work.

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red complex $Os_2(hp)_4Cl_2$ in 84% yield. While we have found that the analogous acetate complex can also be used as the precursor to $Os_2(hp)_4Cl_2$,[7] the yield is appreciably lower than when the butyrate is used. This diosmium(III) complex is the same as that which Cotton and Thompson[13] prepared from the reaction between $OsCl_3$ and 2-hydroxypyridine. Indeed, the electrochemical properties of these materials are the same,[23] an irreversible one-electron oxidation being observed at +1.20 V and a reversible one-electron reduction ($n = 1.05$) at +0.10 V vs. SCE (using a Pt-bead electrode in 0.2 M TBAH–CH_2Cl_2). As was the case with the diosmium(III) carboxylates, we were able to reduce $Os_2(hp)_4Cl_2$ to its monoanion using acetone solutions of cobaltocene, thereby confirming the close electronic relationship between $Os_2(O_2CR)_4Cl_2$ and $Os_2(hp)_4Cl_2$. The olive green complex $[(C_5H_5)_2Co][Os_2(hp)_4Cl_2]$ is much more sensitive to trace amounts of water and oxygen than its carboxylate analogues. Its solution in 0.2 M TBAH–CH_2Cl_2 displays a very characteristic cyclic voltammogram with two one-electron oxidations, with $E_{1/2}$ values of +1.19 and +0.03 V and a couple at −0.90 V vs. SCE due to $(C_5H_5)_2Co^+/(C_5H_5)_2Co$.

The electrochemical and chemical redox behavior we observe for $Os_2(O_2CR)_4Cl_2$ is in accord with that which might be expected on the basis of that for the related ruthenium systems.[9] The difference lies in the greatly enhanced stability of the Ru_2^{5+} core, as is present in $Ru_2(O_2CR)_4Cl$, over that of Ru_2^{6+}; the diruthenium(III) carboxylates $Ru_2(O_2CR)_4Cl_2$ are at present unknown.[24] This trend reflects the general tendency for an increase in the stability of the higher oxidation states as a transition group is descended; i.e. $Os_2^{6+} > Os_2^{5+}$ but $Ru_2^{6+} < Ru_2^{5+}$.

In the case of diruthenium complexes containing the Ru_2^{6+} or Ru_2^{5+} cores, it is apparent that the π^* and δ^* orbitals are close in energy, so that a precise assignment of the electronic structures of such species requires care. Thus, for the carboxylates $Ru_2(O_2CR)_4Cl$, the ground-state configuration is $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*1}$, on the basis of both experimental[9] and theoretical[25] results. On the other hand, the electronic structures of the species $[Ru_2L_2]^+$ and $[Ru_2L_2]^{2+}$, where L represents the dibenzotetraaza[14]annulene $[C_{22}H_{22}N_4]^{2-}$ ligand, are best described in terms of the ground-state configurations $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*1}$ and $\sigma^2\pi^4\delta^2\delta^{*2}$, respectively.[9,26]

For the Os_2^{6+} and Os_2^{5+} cores, as present in the carboxylate complexes, the situation becomes more complicated than this. The magnetic properties of the neutral complexes $Os_2(O_2CR)_4Cl_2$ and $Os_2(hp)_4Cl_2$ ($\mu_{eff} \approx 1.4$–$1.6\ \mu_B/Os_2$ unit at room temperature)[7] indicate that a $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration with an appreciable contribution from the spin-triplet state $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*1}$ may be the best description. When $Os_2(O_2CR)_4Cl_2$ is reduced to its monoanion, we find that the magnetic moment increases. In the case of $[(C_5H_5)_2Co][Os_2(O_2CC_3H_7)_4Cl_2]$, its magnetic moment at 298 K (in CH_2Cl_2 by the Evans method) is $\mu_{eff} \simeq 2.73\ \mu_B$, a value that increases to 2.84 μ_B when the solution is cooled to 209 K. This accords with the configurations $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*2}$ (i.e. three unpaired electrons; cf. Ru_2^{5+}) and $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*1}$ or $\sigma^2\pi^4\delta^2\pi^{*3}$ (one unpaired electron) being the principal contributors to the ground state at room temperature. To further investigate this behavior, we have carried out magnetic measurements on solutions of the electrochemically generated anions. Both the propionate and butyrate $[Os_2(O_2CR)_4Cl_2]^-$ anions were electrogenerated at 0.00 V (vs. a Ag/AgCl reference electrode) at 293 K until such time as the current dropped to <1% of its initial value. The composition of the medium in both cases was 0.5 M n-Bu_4NBF_4 in CH_2Cl_2/CD_2Cl_2 (80/20, v/v). Tetramethylsilane (2%) was added after electrogeneration, and variable-temperature magnetic susceptibilities were determined by the Evans method. Allowance was made for the diamagnetic correction of the ligands and of the solvent. The data in Table I clearly show that, in spite of the technical difficulties involved in the in situ study of the magnetic properties of the air-sensitive electrogenerated diosmium anions, there is rather good agreement with the data obtained for $[(C_5H_5)_2Co][Os_2(O_2CC_3H_7)_4Cl_2]$. The reduced magnetic moments of these $[Os_2(O_2CR)_4Cl_2]^-$ anions and the form of the temperature dependence of μ_{eff} compared to that of isoelectronic $Ru_2(O_2CC_3H_7)_4Cl$ ($\mu_{eff} \approx 4\ \mu_B$/molecule at 300 K)[27] may arise from a larger separation of the π^*/δ^* orbitals in Os_2^{5+}, thereby producing a greater population of the spin-doublet state.

Table I. Magnetic Properties of Electrochemically Generated $[Os_2(O_2CR)_4Cl_2]^-$

R	μ_{eff} (temp)[a]
C_2H_5	2.47 (275), 2.77 (245), 2.88 (215)
C_3H_7	2.65 (240), 2.70 (210), 2.82 (200), 2.85 (190)

[a] μ_{eff} in Bohr magnetons; temperature in Kelvins.

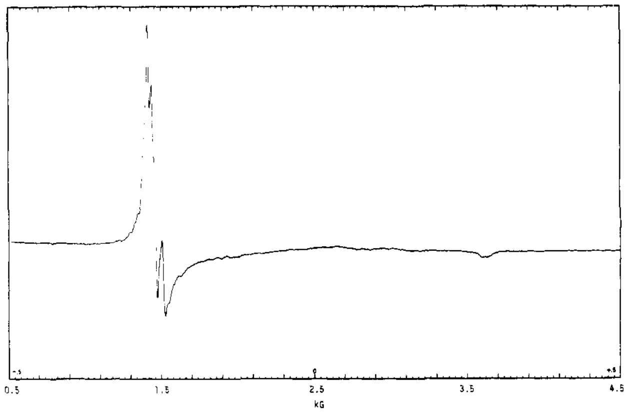

Figure 2. X-Band ESR spectrum of $[(C_5H_5)_2Co][Os_2(hp)_4Cl_2]$ in toluene/CH_2Cl_2 (5/2, v/v) at −160 °C.

A more limited study on $[(C_5H_5)_2Co][Os_2(hp)_4Cl_2]$ revealed that this complex displays comparable behavior.[28] The magnetic moment of this complex (recorded in CH_2Cl_2 by the Evans method) was 2.68 μ_B at 308 K and 2.63 μ_B at 173 K, and while μ_{eff} for this complex did not reveal the same temperature dependence as for $[Os_2(O_2CR)_4Cl_2]^-$, the magnitude of the moment is fully in accord with the population of both $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*2}$, and $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*1}$ (or $\sigma^2\pi^4\delta^2\pi^{*3}$).

The magnetic properties of the Os_2^{5+} complexes indicate that there is a major $S = {}^3/_2$ contribution to the ground state. Consequently, the ESR spectra of these complexes should be similar to that obtained for $Ru_2(O_2CC_3H_7)_4Cl$ by Cotton and Pedersen.[27] These authors concluded that this species exhibits an appreciable zero-field splitting; $2D$ is defined as the separation between the $|\pm{}^3/_2\rangle$ and $|\pm{}^1/_2\rangle$ states at zero magnetic field. If $D > 0$, then the $|\pm{}^1/_2\rangle$ states are lower in energy, while if $D < 0$, then the $|\pm{}^3/_2\rangle$ states are lower. Since spin-orbit coupling for a third-row transition metal is greater than that for the corresponding second-row element, $|2D|$ should then be greater for these Os_2^{5+} complexes as the zero-field

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[23] Cyclic voltammetric data for $Os_2(hp)_4Cl_2$ as prepared from $OsCl_3$ are reported elsewhere: see: Armstrong, J. E. Ph.D. Thesis, Purdue University, 1982; p 79.

[24] Electrochemical studies of $Ru_2(O_2CR)_4Cl$ show that reduction to Ru_2^{4+} is much more favored than oxidation to Ru_2^{6+}.[9]

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[27] Cotton, F. A.; Pedersen, E. *Inorg. Chem.* **1975**, *14*, 388.

[28] We were unable to prepare by electrochemical means a sufficiently pure sample of $[Os_2(hp)_4Cl_2]^-$ to study the magnetic properties of this species when generated in this fashion.

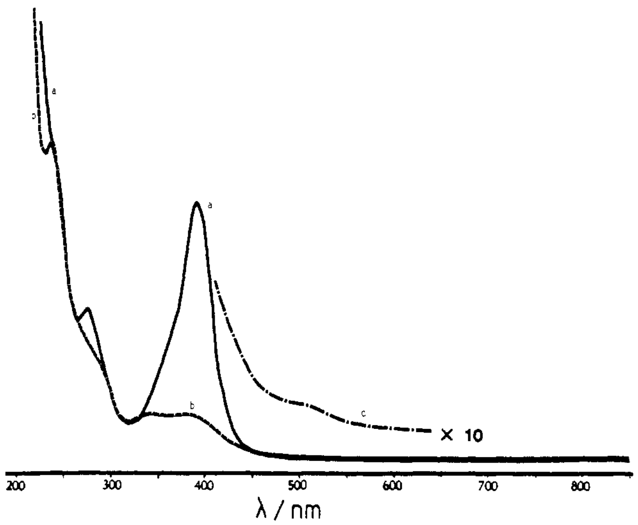

Figure 3. Electronic absorption spectra: (a) $Os_2(O_2CC_2H_5)_4Cl_2$ in 0.5 M n-Bu_4NBF_4-CH_2Cl_2; (b) $[Os_2(O_2CC_2H_5)_4Cl_2]^-$ following its electrochemical generation by electrolysis of solution a at 0.0 V (vs. a Ag/AgCl reference electrode); (c) solution b with a 10-fold increase in concentration. Spectra were recorded at 293 K in an OTTLE cell (with a Pt-gauze working electrode and Infrasil windows).

splitting is a function of the spin–orbit coupling constant. In exploring the X-band ESR spectra of the cobaltocenium salts prepared in the present investigation, we found that the complex $[(C_5H_5)_2Co][Os_2(hp)_4Cl_2]$ exhibits a rather well-defined spectrum in a toluene/dichloromethane glass (5/2, v/v) at −160 °C (see Figure 2).[29] Hyperfine splitting, which we believe is due to ^{14}N of the hydroxypyridinato ligands, is observed for both $g_\parallel$ and $g_\perp$. The g values are $g_\parallel \simeq 2.14$ and $g_\perp \simeq 2.20$, with the magnitude of $A(^{14}N)$ being in the neighborhood of 50 G. A very weak feature at 3600 G is observed in this spectrum and may be due to the parallel orientation lines.[27] These lines are expected to be very weak relative to those centered in the neighborhood of 1500 G.

Spectral simulations of $S = {}^3/_2$ systems by Pedersen and Toftlund[30] indicate that, in the limit of large D values, spectra qualitatively similar to that observed for this complex should be obtained. Indeed, the spectrum of $Ru_2(O_2CC_3H_7)_4Cl$ was fitted by assuming that $|2D|$, the zero-field splitting, was greater than 2.2 cm^{-1}.[26] Accordingly, a similar spectrum might be expected for $[(C_5H_5)_2Co][Os_2(hp)_4Cl_2]$ and related Os_2^{5+} species since the zero-field splitting should be at least as large as that observed for the diruthenium(II,III) complex.

The electrochemical generation of the carboxylate anions $[Os_2(O_2CR)_4Cl_2]^-$ was followed spectroscopically in an OTTLE cell. For the propionate (see Figure 3), the original very strong peak at 392 nm ($\epsilon = 10800$) and shoulder at 360 nm are replaced in the anion by peaks at 380 nm ($\epsilon = 1900$) and 340 nm ($\epsilon = 2000$). In addition, a new weak shoulder appears at 500 nm, the absorption at 277 nm ($\epsilon = 5800$) collapses to a shoulder at ca. 285 nm, and the shoulder at 244 nm becomes a definite peak at 237 nm ($\epsilon = 12000$). In the case of the butyrate complex, very similar changes are observed on one-electron reduction. The strong peak at 392 nm ($\epsilon = 10400$) and shoulder at 364 nm are replaced by bands at 385 nm ($\epsilon = 2600$) and 340 nm ($\epsilon = 3400$). A new weak shoulder appears at 510 nm, and the peak at 278 nm ($\epsilon = 6100$) collapses to a shoulder at ca. 280 nm.[31] Note that these are strictly reversible processes since in each case electrogeneration of the original compounds, with no loss of band intensity, is readily achieved.

A detailed interpretation of these electronic spectra is inappropriate, particularly in view of the uncertainties associated with an exact description of the ground-state composition of both the Os_2^{6+} and Os_2^{5+} cores. However, by analogy with related studies on Ru_2^{5+} carboxylato complexes,[25,33] the main component of the broad absorption band at 392 nm (Os_2^{6+}) and ca. 380 nm (Os_2^{5+}) can probably be assigned to an $O(\pi) \rightarrow Os_2(\pi^*)$ charge-transfer transition. The qualitative observation that the addition of a large excess of n-Bu_4NBr to $Os_2(O_2CC_3H_7)_4Cl_2$ reduces the intensity of the peak at 392 nm and produces an extra peak of comparable intensity at 442 nm suggests that $Cl \rightarrow Os_2(\pi^*)$ charge transfer also occurs in this region.

The profound modification of this prominent charge-transfer absorpion upon reduction from Os_2^{6+} to Os_2^{5+} is as expected for increased occupancy of the diosmium molecular orbital manifold. This behavior and the absence of intervalence bands in the near-infrared region of the Os_2^{5+} system (for both the propionate and butyrate anions no new absorptions with intensities (ϵ) >50 $dm^3\ mol^{-1}\ cm^{-1}$ were observed at wavelengths > 1000 nm) are fully consistent with the delocalized nature we ascribe to the intermediate valence anion. Further discussion of the origin of the other bands in these spectra must be deferred until more experimental and theoretical information such as single-crystal polarized absorption spectra and SCF–Xα–SW calculations is obtained.

The present work, which provides an accurate appraisal of the redox properties of triply bonded diosmium(III) and diosmium(III,II) complexes and their relationship to the analogous diruthenium species, will hopefully serve as an incentive for studies of the redox properties of more exotic diosmium species, such as the fascinating diosmium(II) porphyrin dimers that have been isolated very recently by Collman and co-workers.[34]

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Registry No. $Os_2(hp)_4Cl_2$, 74718-48-2; $[(\eta\text{-}C_5H_5)_2Co][Os_2(O_2CC_3H_7)_4Cl_2]$, 93474-02-3; $[(\eta\text{-}C_5H_5)_2Co][Os_2(O_2CC_2H_5)_4Cl_2]$, 93474-03-4; $[(\eta\text{-}C_5H_5)_2Co][Os_2(hp)_4Cl_2]$, 93529-97-6; $Os_2(O_2CC_3H_7)_4Cl_2$, 83292-95-9; $Os_2(O_2CC_2H_5)_4Cl_2$, 89742-24-5; $(\eta\text{-}C_5H_5)_2Co$, 1277-43-6; Os, 7440-04-2.

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(29) Less satisfactory spectral data were obtained for $[Os_2(O_2CR)_4Cl_2]^-$ and so are not discussed here. While the signals were much weaker than were those of the 2-hydroxypyridine complex, we note that the X-band ESR spectra of $[(C_5H_5)_2Co][Os_2(O_2CC_3H_7)_4Cl_2]$ and electrochemically generated $[Os_2(O_2CC_3H_7)_4Cl_2]^-$ were, as expected, identical. The spectra were recorded at −160 °C on toluene/CH_2Cl_2 (5/2, v/v) solutions and show two reasonably intense signals at 2460 and 2840 G, with a weaker feature at 4600 G. It may be that differences between the ESR spectra of $[Os_2(hp)_4Cl_2]^-$ and $[Os_2(O_2CR)_4Cl_2]^-$ reflect a change in the sign of the zero-field splitting parameter. This may also explain the differences in the temperature dependence of the magnetic moments of these complexes.

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(31) Similar spectral features were observed upon measuring the electronic absorption spectra of $[(C_5H_5)_2Co][Os_2(O_2CC_3H_7)_4Cl_2]$, although in this instance allowance has to be made for cobaltocenium absorptions.[32] Dichloromethane solutions of this salt show bands at 348, 393, and 510 (sh) nm that clearly have counterparts in the spectra of the electrochemically generated samples. Also, two much weaker features were observed at ~620 (br, sh) and ~850 nm, both possessing $\epsilon \lesssim 100$.

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