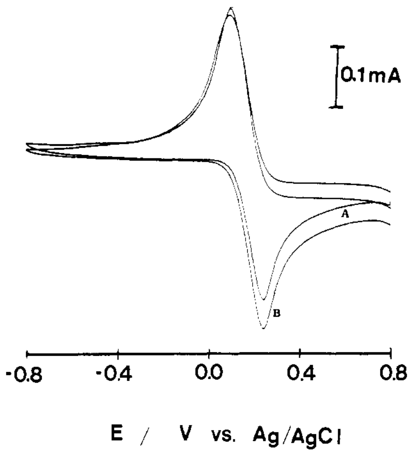

Figure 6. Cyclic voltammogram of a polymer-modified electrode with $Ni(mnt)_2^{2-}$ in contact with 2×10^{-3} M $Fe(CN)_6^{3-/4-}$ in 1.0 M KCl (A) in the dark, and (B) under visible light illumination. Scan rate = 5 mV/s. Anodic currents are downward.

The slow response of the system is associated with the diffusion coefficients approximately for the Fe couple obtained in the chronoamperometric experiments.

The fact that the nickel and platinum complexes are electroinactive in the composite film is quite surprising. This contrasts the results of the complex incorporated by ion exchange in the QPVP films.[4] The method of preparation in the latter case differs from the present preparation of the polymer film composites. The metal maleonitriledithiolate complexes appear to be bound by strong electrostatic interactions to the quaternized alkyl ammonium sites in the copolymer moiety of the polymer blend. Axial ligation of the complex to pyridine sites of the poly(vinylpyridine) moiety of the blend should not be discounted as possible binding sites for the strongly colored complexes. The photoresponse of the system is complex, and a mechanism of charge transport is not clear.

The puzzle presented by the mechanism is how the electron is transported from the excited $Ni(mnt)_2^{2-}$ complex to the SnO_2 electrode. Two possibilities present themselves. One is energy migration from the point of excitation to the interface, with charge separation being limited to the interface. This seems unlikely. Earlier reports indicate short excited-state lifetimes for the complex,[3,10] and it is difficult to see how an exciton mechanism can be consistent with upward curvature of the current–intensity curve. The other possibility is that the excited state of $Ni(mnt)_2^{2-}$ transfers an electron to π^* levels of an aromatic ring of the polymer and that transfer to the electrode is an analogue of conductivity in polystyrene after electron injection.[11] This mechanism is energetically allowed on the basis of the energy of the lowest lying excited state of the complex and the reduction potential of aromatic groups. The ^1A_g ground state of the $Ni(mnt)_2^{2-}$ complex is located at −0.1 V versus NHE. The reduction potential of the pyridinium group lies at −0.45 V versus NHE. Excitation to the lowest excited state of the complex adds 3.06 eV of photon energy to the reduction power, making transfer to the pyridinium group thermodynamically feasible.

Further support for this mechanism comes from the wavelength dependence of photocurrents in a similar phthalocyanine film to be reported elsewhere.[12] In this mechanism, the slow response would be related to trap-controlled charge migration in this film. The magnitude of the photoresponse is dependent on the energetics of charge transfer, the lifetime of the excited state (in this case, the picosecond domain), and the polymer morphology. The highly disordered amorphous nature of this film can give rise to a large number of localized states.

Figure 6 shows a cyclic voltammogram of the electrode under illumination that foreshadows use of as a photoswitch or photodiode-like device. At potentials between 0.1 and 0.8 V vs Ag/AgCl, the dark currents are small and irradiation in the milliwatt per square centimeter range can turn on a current of several microamperes. The larger anodic photocurrents are in agreement with the proposed mechanism in Scheme I. Localized energy states in the polymer film at these potentials may be slightly altered to allow for greater conduction of charge through the polymer film.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council (NSERC) and Actions Structurantes for financial support.

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Nitrile Complexes of Pentaammineosmium(II) and -(III)

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Earlier work on nitrile complexes of $(NH_3)_5Os^{2+}$ and $(NH_3)_5Os^{3+}$ has been extended to include as ligands nitriles ($RC{\equiv}N$) that are stronger π acids. There is a progressive decrease in the $C{\equiv}N$ stretching frequency for the Os(II) complexes along the series R = CH_3, $CH_2{=}CH$, C_6H_5, C_6F_5. The same order is observed for the Os(III) species, supporting the conclusion that back-bonding is significant also for Os(III). For the complexes of the nitriles with R = C_6H_5, C_6F_5, and $C_{14}H_9$ (9-anthracene), two absorption bands are observed in the visible region at energies below those attributable to the ligand itself, which are assigned to MLCT. For Os(III), at the present level of refinement, only when R = $C_{14}H_9$ do the UV-visible spectra reveal interesting features. There is a prominent peak at 453 nm, which we assign to MLCT. At still lower energies, a progression of peaks, with separations suggesting a vibrational component, is observed, which we tentatively ascribe to a ligand-centered singlet–triplet transition induced by the paramagnetic metal ion. When the complex of C_6H_5CN is prepared by the reaction of $(NH_3)_5Os^{II}$ with the ligand, two forms are observed. The minor component, in which the metal is bound to the ring in an η^2 mode, is thought to rearrange slowly to the major N-bound form, by an intramolecular mechanism.

Introduction

Nitriles have figured prominently[1] in the development of the chemistry of ruthenium ammines. In line with our current program of exploring the chemistry of the pentaammineosmium moiety, where complexes of Os(II) with π-acid ligands appeared to be of special interest, we undertook to prepare and characterize some (nitrile)pentaammineosmium complexes. Several, including that with the acetonitrile as the heteroligand, had already been characterized in our laboratories.[2] In view of the evidence

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(1) Clarke, R. E.; Ford, P. C. *Inorg. Chem.* **1970**, *9*, 227.

(2) Work mainly by P. A. Lay, in preparation for publication.

0020-1669/88/1327-3604$01.50/0

Table I. Conditions of Preparations

amt of Os(III), mmol	ligand (amt, mmol)	solvent (amt, mL)	temp, °C	time, h	% yield of final product
0.55	CH_3CN[a]	CH_3CN (35)[a]	50	3	72
0.14	C_2H_5CN (0.042)	PC[b] (3)	50	3	53
0.28	$(CH_3)_3CCN$ (0.036)	Ac[b] (8)	60	18	96
0.28	$CH_2{=}CHCN$ (0.061)	Ac (4)	RT[d]	65	97
0.69	C_6H_5CN (1.27)	Ac (20)	RT	38	91
0.28	C_6F_5CN (0.016)	PC (4)	60	65	92
0.28	9-ACN[c] (0.0083)	Ac (10)	65	120	74

[a] Ligand is the neat solvent. [b] PC ≡ propylene carbonate; Ac ≡ acetone. [c] 9-ACN ≡ 9-anthracenecarbonitrile. [d] Room temperature.

provided by this earlier work that back-bonding is significant even for the Os(III) complexes, there was interest in extending the investigation to nitriles that are stronger π acids. The interest in further work on the nitrile complexes intensified as a result of the finding[3,4] that $(NH_3)_5Os^{II}$ has a great propensity for interacting with unsaturated ligands in the η^2 mode. On the basis of the earlier work, there was no reason to believe that any of the nitriles which already had been used attached themselves to $(NH_3)_5Os^{II}$ in any other than the orthodox fashion. It did however seem possible that when the nitrile function is activated by a suitable electron-withdrawing group, the η^2 binding mode would be preferred. This has not proven to be the case for any of the nitriles described in this paper. Of those we tried, one of the best prospects for η^2 ligation is CF_3CN, but our attempts to prepare the complex with $(NH_3)_5Os^{II}$ were vitiated by side reactions. There is ample precedent in the literature for the η^2 binding mode for activated nitriles,[5,6] and in fact, since we began our work, a complex that features even CH_3CN in this binding mode has been reported.[7]

Experimental Section

Preparation of the Nitrile Complexes. The salt $[Os(NH_3)_5O_3SCF_3](CF_3SO_3)_2$, prepared as described in the literature,[8] was dissolved in neat nitrile (method used for acetonitrile) or in a poorly coordinating solvent such as acetone or propylene carbonate, containing an excess of the entering nitrile, the reaction mixture being kept at a suitable temperature until reaction was complete. The progress of the reaction was monitored by cyclic voltammetry on aliquots of the reaction mixture dissolved in "glyme". "Complete" corresponds to the absence of the redox wave characteristic of the starting material (this appears at $E \sim -0.75$ V (NHE)). Solids were precipitated by adding ether to the product solution and were recrystallized from acetone by vapor diffusion of ether. A range of concentrations and reaction times was used; specific details for each kind of preparation are summarized in Table I.

Pentaammineosmium(II) nitrile comlexes were obtained by reducing the corresponding Os(III) nitrile species with Mg turnings in acetone under argon. In a typical preparation 300 mg of the Os(III) salt was dissolved in 10 mL of acetone and 1 g of Mg turnings was added. The mixture was stirred for 1–2 h at room temperature, the progress of the reaction being followed by cyclic voltammetry. The solid was recovered and purified as described for the Os(III) salts.

Table II. Reduction Potentials of the $[Os(NH_3)_5NCR]^{3+/2+}$ Couples

R	$E_{1/2}$, V (NHE)[a]	R	$E_{1/2}$, V (NHE)[a]
CH_3	−0.29	C_6H_5	−0.19
CH_3CH_2	−0.35	C_6F_5	0.09
$C(CH_3)_3$	−0.33	$C_{14}H_9$	−0.10
$CH_2{=}CH$	−0.17		

[a] Recorded in 0.50 M $NaCF_3SO_3$/glyme solution at 200 mV/s.

Results

Cyclic voltammograms run on the preparations showed no hint of electroactive response other than that attributable to the desired material over the range +1.0 to −1.5 V (NHE), and on this basis we estimate the content of other osmium-containing impurities to be less than 3%. The results of the cyclic voltammetry experiments are summarized in Table II.

The IR spectra were obtained on samples pelletized in KBr, the measurements being made on an IBM98 FTIR instrument. The results in the region of the CN stretching frequency are summarized in Table III, together with relevant data gathered from the literature.

In Tables IV and V are summarized the data on the spectrophotometric measurements for the UV–vis region of the spectra, and in Table VI, those for the Os(III) species in the near-IR region.

When $[Os(NH_3)_5(CF_3SO_3)]_3$ is reduced in the presence of excess benzonitrile,[16] two structural forms of $[Os(NH_3)_5(PhCN)]^{2+}$ are obtained. Our attempts to separate these species were unsuccessful. Although the major component of this mixture exhibits nitrile coordination, NMR, IR, and electrochemical data indicate that about 15% of the complex exists as an η^2-arene isomer. A ^1H NMR spectrum of the mixture displays cis- and trans-ammine resonances at 3.70 and 4.95 ppm, respectively, accompanying the proton signals associated with the nitrile species.[17] Otherwise, at room temperature, the aromatic region is practically featureless, showing only a broad resonance at 6.9 ppm. Upon cooling of the sample to −60 °C, this signal is replaced by multiple resonances over the range 8.0–5.3 ppm, thought to be associated with the ring protons. Though decoupling experiments failed to provide a conclusive structural assignment at this temperature, the features observed are similar to those seen with other $[Os(NH_3)_5(\eta^2\text{-}PhR)]^{2+}$ systems[4,18] and indicate that the π-arene isomer is fluxional at room temperature. An IR spectrum of the mixture recorded as a glaze on a NaCl salt plate features C–N stretches at 2144 and 2216 cm^{-1}, the latter of which we assign to the arene isomer. Though this value is close to that for the free ligand, the shift toward lower energy probably reflects a decrease in the benzonitrile π-electron density, attributable to metal back-bonding. The cyclic voltammogram[19] of the isomer mixture in acetone exhibits a chemically irreversible oxidation wave at $E_p = 0.48$ V (NHE), this value appearing over 600 mV positive to the reversible couple characteristic of the major component ($E_{1/2} = -0.15$ V in acetone). Relative to the parent complex $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+}$, the 2+/3+ couple of the benzonitrile derivative is estimated to be about 200 mV positive, a value that is in good agreement with those of other substituted-benzene complexes that employ electron-withdrawing substituents.[18] The subsequent cathodic scan reveals a wave at −0.45 V, which is absent prior to oxidation of the arene isomer. This value is consistent with the reduction of $[Os(NH_3)_5(CH_3)_2CO]^{3+}$ and indicates that $[Os(NH_3)_5(\eta^2\text{-}PhCN)]^{3+}$ is unstable with respect to the displacement of the nitrile by solvent.[3] In contrast, $[Os(NH_3)_5(\eta^2\text{-}PhCN)]^{2+}$ is quite stable toward solvolysis: cyclic voltammograms of the isomer mixture recorded over a 3-day

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(14) Sen, J.; Taube, H. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 125.
(15) For anthracene, the lowest triplet state is 14.9 × 10^3 cm^{-1} above the ground state, corresponding to absorption at 671 nm: Kellogg, R. E. *J. Chem. Phys.* **1966**, *44*, 411.
(16) $Os(NH_3)_5(CF_3SO_3)_3$ is reduced in a cosolvent mixture of DME and DMA. The product solution is filtered and treated with excess CH_2Cl_2 to precipitate the final solid.
(17) ^1H NMR spectrum of $[Os(NH_3)_5NCPh]^{2+}$ recorded in acetone (ppm): 3.87 (b, 12 H), 4.09 (b, 3 H), 7.52 (d, 2 H), 7.38 (m, 2 H), 7.40 (m, 1 H).
(18) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.*, in press.
(19) Scan rate 100 mV/s; 1 M TBAH solution.

Table III. Nitrile Stretch Vibrations (cm^{-1})

R	free ligand	Os(II)^{a,b} ($\Delta\nu$)	Os(III)^{a,b} ($\Delta\nu$)	Ru(II)^{a} ($\Delta\nu$)	Ru(III)^{a} ($\Delta\nu$)	Rh(III)^{a} ($\Delta\nu$)
CH_3	2254^{e}	2191 (−67)	2298 (+44)	2239 (−15)^{b,e}	2286 (+32)^{b,e}	2323 (+69)^{c,g}
CH_3CH_2	2248^{h}	2198 (−50)	2285 w (+37)			
$C(CH_3)_3$	2237^{h}	2171 (−66)	2261 w (+24)			
$CH_2{=}CH$	2228^{f}	2138 (−90)	2250 w (+22)	2184 (−44)^{c,f}	2267 (+39)^{c,f}	2288 (+60)^{c,g}
C_6H_5	2231^{g}	2144 (−87)	2246 (+15)	2188 (−43)^{c,e}	2267 (+36)^{c,e}	2287 (+56)^{c,g}
C_6F_5	2214	2121 (−93) (2094 (−120))	(2209 (−5)) 2197 (−17)			
$C_{14}H_9$	2246^{e}	2127 (−119)	2261 w (+15)	2189 (−57)^{d,e}		

[a] $[M(NH_3)_5NCR]^{n+}$ (n = 2, 3). [b] $CF_3SO_3^-$ salt. [c] BF_4^- salt. [d] ClO_4^- salt. [e] Br^- salt. [f] Reference 1. [g] Reference 9. [h] Aldrich.

Table IV. UV–Visible Spectral Data for the Os(II)–Nitrile Complexes $[Os(NH_3)_5(RCN)](CF_3SO_3)_2$^{a}

R	λ_{max}, nm ($10^{-3}\epsilon$)^{b}
CH_3	231 (20), 313 (sh), 393 (sh)
CH_3CH_2	235 (19), 312 (sh), 395 (sh)
$C(CH_3)_3$	236 (21), 312 (sh), 398 (sh)
C_6H_5	239 (18), 258 (sh), 290 (sh), 403 (10), 509 (3.4)
C_6F_5	252 (18), 280 (18), 377 (sh), 437 (9.2), 567 (2.8)
$C_{14}H_9$	253 (130), 288 (15), 355 (sh), 374 (6.7), 396 (sh), 534 (11), 703 (4.5)

[a] In CH_3OH at room temperature. [b] Values subject to 10% error.

Table V. UV–Visible Spectral Data for the Os(III)–Nitrile Complexes $[Os(NH_3)_5(RCN)](CF_3SO_3)_3$^{a}

R	λ_{max}, nm ($10^{-3}\epsilon$)^{b}
CH_3	<210; 257 (sh) (0.93); 323 (sh) (0.045)
CH_3CH_2	<210; 257 (sh) (0.81); 325 (sh) (0.040)
$C(CH_3)_3$	<210; 257 (sh) (1.1); 325 (sh) (0.085)
$CH_2{=}CH$	261 (5.4); 284 (sh) (4.6); 326 (sh) (1.2)
C_6H_5	223 (13); 275 (sh) (9.1); 281 (9.4); 290 (sh) (9.3); 338 (sh) (1.1); 361 (sh) (0.50); 330 (sh) (1.9)
C_6F_5	264 (6.9); 410 (sh) (0.19); 427 (sh) (0.12)
$C_{14}H_9$	261 (110); 306 (sh) (3.1); 312 (sh) (2.9); 333 (sh) (2.2); 351 (sh) (4.5); 369 (83); 391 (9.3), 414 (11), 453 (6.5), 505 (0.75); 544 (0.82); 588 (0.66); 639 (sh) (0.12); 697 (0.11); 772 (0.06)

[a] In 0.1 M CF_3SO_3H/CH_3OH solution at room temperature. [b] Values quoted are subject to error of 10%.

Table VI. λ_{max} of $[Os(NH_3)_5(RCN)](CF_3SO_3)_3$ Complexes in the Near-IR Region^{a}

R	λ_{max}		R	λ_{max}	
	nm	cm^{-1}		nm	cm^{-1}
CH_3	2069	4833	C_6H_5	2096	4771
CH_3CH_2	2070	4831	C_6F_5	2116	4726
$C(CH_3)_3$	2075	4819	$C_{14}H_9$	2141	4671
CH_2CH	2092	4780			

[a] Recorded as KBr pellets.

period in acetonitrile reveal a slow decay of the complex without the appearance of another electroactive species. Our interpretation of these findings is that the arene complex converts to the thermodynamically favored nitrile isomer. The absence of the substitution-inert species $[Os(NH_3)_5CH_3CN]^{2+}$ suggests an intramolecular rearrangement.

Discussion

Nitrile Stretching Vibrations. Of all the metal ions featured in Table III, Rh(III)(π d^6) has the least complex effect on the nitrile frequencies, and even here two factors need to be taken into account: the purely kinematic one of attaching a heavy atom to the nitrile and an electronic effect arising from the σ bond between the metal atom and the nitrogen of the nitrile group. The purely kinematic effect will not be significantly different for Ru(III)(π d^5), nor is the purely σ-bond strength expected to be much different. Ruthenium(III), however, consistently shows a smaller value of $\Delta\nu$, which calls for comment. The major π interaction for Ru(III) with the nitriles is quite likely $\pi d \leftarrow \pi$ charge transfer, and it seems reasonable to attribute the smaller value of $\Delta\nu$ for Ru(III) as compared to that for Rh(III) to the attendant weakening of the C–N π bond.

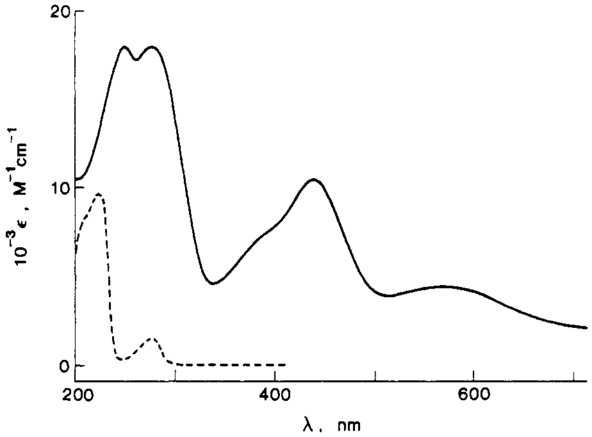

Figure 1. UV–visible spectra for $[Os(NH_3)_5(C_6F_5CN)](CF_3SO_3)_2$ (—) and C_6F_5CN (---) in methanol.

For Os(III), as the observations on the absorption in the UV–visible region will be shown to suggest, the major π effect involves charge transfer from the metal ion to the ligand, and in fact differences in reactivity[2] between nitriles coordinated to Ru(III) and to Os(III) also support the idea that Ru(III) tends to extract extra electron density by LMCT, while Os(III) contributes extra electron density by MLCT.

As is better documented by the values of $\Delta\nu$ for the lower oxidation states, back-bonding also decreased the value of $\Delta\nu$. For Ru(II) and Os(II) the dominant effects are due to back-bonding, the latter consistently showing a greater influence than the former.

As to differences between ligands, both inductive effects (C_6F_5 compared to C_6H_5) and resonance effects (9-anthracene compared to C_6H_5) contribute to enhancing the effect of back-bonding in decreasing the C≡N stretching frequency.

UV–Visible Absorption. Os(II) Complexes. The strong absorptions at shorter wavelength (231, 235, and 236 nm for R = CH_3, CH_3CH_2, and $C(CH_3)_3$, respectively) can be attributed to $\pi^* \leftarrow \pi d$ charge transfer. The shoulders at shorter wavelength are unassigned, but it should be noted that one of them may be the result of a d–d transition.

For the three complexes featuring aromatic nitriles, in each case there are two well-resolved bands at energies lower than corresponds to absorption by the ligand itself. The fact that the intensity ratios are similar (ranging from 3 to 4 for the higher energy compared to the lower) suggests that they have a similar origin, as does the fact that the splittings 5.1×10^3, 4.7×10^3, and 4.3×10^3 cm^{-1} for C_6H_5, C_6F_5, and $C_{14}H_9$, respectively, constitute a reasonable progression, in the sense that the energies of the transition are similarly ordered (Figures 1 and 2). A weaker band on the low-energy side of the major charge-transfer transition has been observed[11] for (μ-dinitrogen)bis(pentaammineosmium(II)) and for the complexes of pentaammineosmium(II) with nitrogen heterocyclics.[12] They appear also in certain pentaammineruthenium(II) complexes with some ligands. These low-energy transitions have been attributed[12] to a symmetry-allowed charge-transfer transition, which has low intensity because of poor overlap, but this assignment was not persuasively made. In a more

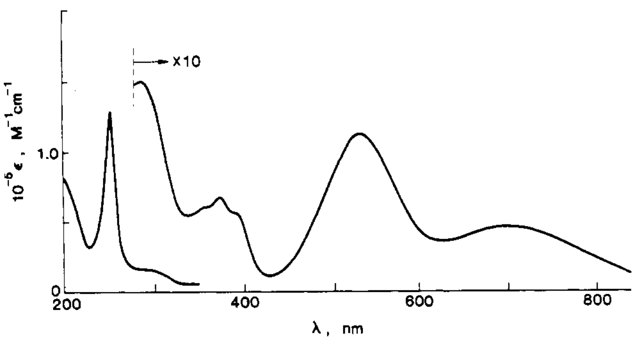

Figure 2. UV-visible spectrum for $[Os(NH_3)_5(C_{14}H_9CN)](CF_3SO_3)_2$ in methanol.

recent paper,[13] experimental evidence was adduced that proved them to be charge transfer in nature, lending some support to the original assignment. Our new data on the low-energy bands again cloud the issue. Whereas, in the systems dealt with in the paper by Creutz and Chou,[13] the energy separations increase as the band energy decreases, consistent with the view that the low-energy band arises from a ground-state level unaffected by back-donation, in our system, the energy separations decrease with the band energies.

It should be noted that the UV-visible spectra of two of the Os(II) complexes we studied were recorded in earlier work.[2] The earlier observations on the two low-energy bands for the benzonitrile complex agree quantitatively with those reported here. This is not true however for the data for the acetonitrile complex, where for a solution in water the characteristics reported are as follows [λ, nm (ε)]: 228 (1.2×10^4), 280 sh (3.2×10^3), 320 sh (1.2×10^3), 390 sh (2.0×10^2). The internal agreement of the spectra (in CH_3OH) reported here for the three different alkanenitriles suggests that there may be a solvent effect, especially noticeable in the high-energy transitions.

Os(III) Complexes. Metal to ligand charge transfer (MLCT) has been invoked[14] to interpret the near-UV absorption of N-heterocyclic complexes of pentaammineosmium(III). This absorption gives rise to two bands, split by about 6×10^3 cm^{-1}. The separation was attributed in the referenced paper to the effects of spin-orbit coupling and erroneously associated with Os(III) rather than with Os(IV), which is the product of the MLCT.

The spectra of the Os(III) complexes of the three alkanenitriles show shoulders at 257 ± 2 and 325 nm, which are not attributable to the ligands themselves. These shoulders appear as weak features on sharply rising absorption at energies below that shown by the free ligand. The strong absorption presumably is the major charge-transfer band, the maximum for which lies outside the range of our equipment. As to the shoulders themeselves: one at least is likely, a d-d transition. The fact that the energy separation for neither, as compared to the case of the strong transition, corresponds to that observed for N-heterocyclic complexes casts doubt on the interpretation advanced in ref 14.

For the nitriles shown in Table VI, leaving aside for the time being the complex of 9-cyanoanthracene, the interpretation of the spectra in the high-energy region is complicated by absorption by the ligands themselves, this absorption being subject to influences by the metal ions that can affect both intensities and energies in ways that are not understood. In every case, weak features are observed in the low-energy regions, where the ligands themselves show no absorption. In the case of all of these complexes, some appear at energies so low that they cannot be assigned to d-d transitions, but their origin at this writing is obscure.

The most striking observations are those made with the complex of 9-cyanoanthracene (Figure 3). All of the features beginning at 414 nm and continuing to shorter wavelength, with the exception of the weak absorptions in the range 306-333 nm, can be assigned as intraligand in origin. The prominent band at 453 nm ($\epsilon = 6.5 \times 10^3$) we assign to a MLCT. Less obvious is the assignment of the band progression observed at lower energy where six maxima can be identified, separated by a common energy interval, (1.2- to 1.3) $\times 10^3$ cm^{-1}. It is unlikely that this is related to spin-orbit coupling in osmium, because a qualitatively similar feature is observed for the complex with $(NH_3)_5Ru$,[20] where the spin-orbit coupling constant, whether for Ru(III) or Ru(IV), is much smaller than for osmium. The ruthenium complex was prepared on the basis of the theory that the progression at low energy observed for the osmium complex arises from a singlet-triplet transition in the ligand induced by the paramagnetic ion. It should be noted that anthracene itself has the lowest singlet-triplet transition at 671 nm.[15] The fact that the wavelengths of the 0-0 bands for the two species—770 nm for Os(III) and 800 nm for Ru(III)—are so nearly the same suggests a common origin for the absorption in this region. There are however marked differences in relative intensities as the energy changes. These may be related to the differences in the mechanism of electron delocalization from the metal to the ligands in the two cases. In taking into account also the evidence from other systems, we assign the major charge-transfer band at 517 nm for $(NH_3)_5Os^{III}$ to MLCT.[14]

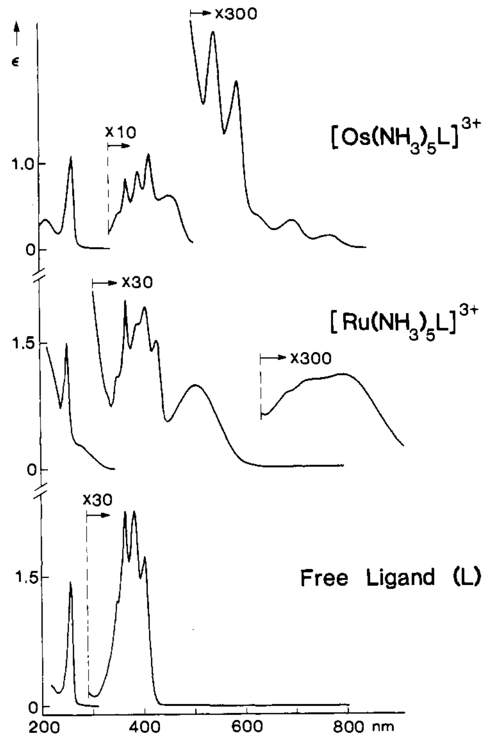

Figure 3. UV-visible spectra for 9-cyanoanthracene and corresponding M(III) complexes.

The near-IR region for the Os(III) complexes reveals the spin-orbit transitions of the cation. Because the spectra were obtained in pellets, no attempt was made to determine extinction coefficients though, in view of the trend in λ_{max} to lower energies as the strength of the π-acid ligand increases, such data would be of interest. The trend referred to is consistent with there being increased metal to ligand delocalization along the series.

Reduction Potentials. There is little to comment on the redox potentials that we have recorded. There is a consistent trend toward increasing values of the formal potentials as the extent of electron delocalization increases. Though MLCT is invoked also for Os(III), the effect on the Os(II) state is expected to dominate, Os(II) being stabilized relative to Os(III) along the series. The only significant exception to the trend referred to is in the case of C_6F_5CN as ligand. Here the σ bond to the ligand becomes a factor. The fluorinated radical does cause a lowering of the π* orbital, but it also makes the ligand less basic. This effect will be more pronounced in the stronger Lewis acid, Os(III), than in Os(II), thus destabilizing the former compared to the latter.

It may be worth pointing out that these osmium complexes have proven useful in our work as strong outer-sphere reducing agents

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(20) λ, nm ($10^{-3}\epsilon$): 253 (153), 280 (30), 398 (3.8), 366 (6.7), 390 (5.8), 403 (6.4), 426 (5.1), 500 (3.4), 800 (0.3).

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and may find applications in other systems because of the potential range they cover.

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Registry No. $[Os(NH_3)_5O_3SCF_3](CF_3SO_3)_2$, 83781-30-0; $[Os(NH_3)_5CH_3CN](CF_3SO_3)_2$, 109242-81-1; $[Os(NH_3)_5C_2H_5CN](CF_3SO_3)_2$, 116232-04-3; $[Os(NH_3)_5(CH_3)_3CCN](CF_3SO_3)_2$, 116232-06-5; $[Os(NH_3)_2CH_2{=}CHCN](CF_3SO_3)_2$, 116232-08-7; $[Os(NH_3)_5C_6H_5CN](CF_3SO_3)_2$, 113161-74-3; $[Os(NH_3)_5C_6F_5CN](CF_3SO_3)_2$, 113161-76-5; $[Os(NH_3)_5(9\text{-}ACN)](CF_3SO_3)_2$, 116232-10-1; $[Os(NH_3)_5CH_3CN](CF_3SO_3)_3$, 83781-33-3; $[Os(NH_3)_5C_2H_5CN](CF_3SO_3)_3$, 116232-12-3; $[Os(NH_3)_5(CH_3)_3CCN](CF_3SO_3)_3$, 116232-14-5; $[Os(NH_3)_5CH_2{=}CHCN](CF_3SO_3)_3$, 116232-16-7; $[Os(NH_3)_5C_6H_5CN](CF_3SO_3)_3$, 116232-17-8; $[Os(NH_3)_5C_6F_5CN](CF_3SO_3)_3$, 116232-19-0; $[Os(NH_3)_5(9\text{-}ACN)](CF_3SO_3)_3$, 116232-21-4.

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Technetium Electrochemistry. 6.[1] Electrochemical Behavior of Cationic Rhenium and Technetium Complexes in Aqueous and Aqueous Micellar Solutions

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The behavior of the M(III/II) redox couple of a number of technetium(III) and rhenium(III) complexes of the general formula *trans*-$[MD_2X_2]^+$, where D is 1,2-bis(diethylphosphino)ethane (depe) or 1,2-bis(dimethylphosphino)ethane (dmpe) and X is Cl or Br, has been investigated by cyclic voltammetry, chronocoulometry, and square-wave voltammetry in aqueous solution and in aqueous media that contain anionic (SDS), cationic (CTAB), or nonionic (Triton X-100) surfactants. In aqueous solution, insolubility of the electrogenerated *trans*-$[M^{II}D_2X_2]^0$ complex results in adsorption at a glassy-carbon electrode for all complexes. However, ionic surfactants effectively solubilize the $[M(dmpe)_2X_2]^0$ species such that diffusion-controlled reversible cyclic voltammograms are observed in these media. In contrast, the more lipophilic $[M(depe)_2Cl_2]^+$ complexes behave differently in that while the solubility of the cationic M(III) complexes is enhanced in the surfactant media, the electrogenerated neutral M(II) complexes are adsorbed on the electrode surface. These observations are qualitatively discussed in terms of the net stabilization of the components of the M(III/II) redox pair in the various surfactant media. This stabilization is primarily dependent on (i) the formal charge on the electroactive complex (cationic vs neutral), (ii) the formal charge on the surfactant molecule that forms the micelle (anionic, cationic, or neutral), and (iii) the lipophilicity of the components of the redox couple (dmpe or depe) and somewhat dependent on the chemical nature of the ions from the supporting electrolyte.

Introduction

Electrochemical techniques are important to the characterization of new inorganic complexes. Voltammetric methods allow for the assignment of oxidation states, assessment of chemical stability, and measurement of formal redox potentials, $E^{\circ\prime}$, of reversible redox couples. The development of cationic technetium-99m complexes as potential myocardial imaging agents[2-5] has especially benefited from applications of electrochemical and spectroelectrochemical techniques.[3,6-9] For example, several series of analogous technetium-99 and rhenium complexes that incorporate tertiary phosphine or arsine ligands have been synthesized in macroscopic amounts and characterized by physical methods, including electrochemistry.[3,6-9] Systematic variation in the redox properties of these complexes is achieved by judicious choice of the donor properties of the coordinating ligands. The information obtained from the physical characterization of the ^{99}Tc and Re complexes, combined with complementary biodistribution studies, is useful in unraveling the complicated biological behavior of the analogous ^{99m}Tc species. In fact, such studies have shown that the in vivo redox fate of these complexes is an important criterion in determining their potential utility as organ imaging agents.[8,9] Thus, structure and redox reactivity studies in combination with biodistribution data form an important basis for the development of more effective technetium and rhenium radiopharmaceuticals.[9]

Previous electrochemical studies of technetium and rhenium complexes have focused on the characterization of their redox properties in nonaqueous solvents.[3,10-14] While chemically useful, the results of these nonaqueous studies are not directly relevant to the biological environment encountered by ^{99m}Tc myocardial imaging agents. In an effort to examine the redox behavior of cationic coordination complexes of the type *trans*-$[M^{III}D_2X_2]^+$ (where D is a bidentate ditertiary phosphine ligand and X is a halide or pseudohalide ligand) in more biologically relevant media,

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