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Mixed-Valence Molecules Based on Monohydridobis(ethylenediamine)osmium(IV) and Metal Cyano Complexes

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The affinity in water of $[Os(en)_2(\eta^2\text{-}H_2)H_2O]^{2+}$ for $Fe(CN)_6^{4-}$—and for the other cyano complexes featured in this report—is high, and upon mixture of the reagents $[Os(en)_2(\eta^2\text{-}H_2)Fe(CN)_6]^{2-}$ (Os(II)–Fe(II)) forms rapidly. On exposure of the colorless solution to air, it rapidly turns blue, as is the case also with $S_2O_8^{2-}$ or $FeCp_2^+$ as oxidant. The full development of the color ($\lambda_{max} = 660$ nm, $\epsilon = (2.1 \pm 0.1) \times 10^3$ M^{-1} cm^{-1}) requires 2 equiv of oxidant/mol of Os(II)–Fe(II). Spectrophotometric and other evidence leads to the conclusion that the product is $[Os^{IV}(en)_2(H)(Fe^{II}(CN)_6)H_2O]$ (Os(IV)–Fe(II)). It is formed also from $[Os(en)_2(H)(H_2O)_2]^{3+}$, as already reported,[3] and $Fe(CN)_6^{4-}$. By the latter method of preparation, it is difficult to separate the formation of Os(IV)–Fe(II) from a following reaction, which leads to a doubling of ϵ, with little shift in λ_{max}, and which we attribute to polynuclear formation. In the presence of $Fe(CN)_6^{4-}$ in excess of 2:1, ϵ rises to 4.4×10^3 M^{-1} cm^{-1} and λ_{max} shifts to 682 nm. Both observations lend weight to the conclusion[3] that the metal center in the residue $[Os^{IV}(en)_2H]^{3+}$ can assume a coordination number of 7. The products of the $2e^-$ oxidation of the complexes formed when $[Os(en)_2(\eta^2\text{-}H_2)H_2O]^{2+}$ reacts with $Os(CN)_6^{4-}$ and $Ru(CN)_6^{4-}$ have the following respective absorption characteristics: $\lambda_{max} = 592$ nm, $\epsilon = 2.2 \times 10^3$ M^{-1} cm^{-1}; $\lambda_{max} = 522$ nm, $\epsilon = 1.9 \times 10^3$ M^{-1} cm^{-1}. The trend in λ_{max} with the value of $E°$ for the three $M(CN)_6^{3-/4-}$ couples and the characteristics of the absorption band indicate that the mixed-valence molecules are localized and that the absorption bands are associated with $M(CN)_6^{4-} \rightarrow Os(IV)$ electron transfer. For $Mo(CN)_8^{4-}$ as nucleophile, λ_{max} appears at 702 nm. The lower energy of the transition compared to that for Os(IV)–Fe(II) is ascribed to a lower Franck–Condon barrier to electron transfer for the octacyano complex. Association of $Fe(CN)_6^{3-}$ with the Os(IV) center also gives rise to charge transfer absorption, with characteristics much like those observed for Os(IV)–Fe(II), but which must now involve Os(IV) to $Fe(CN)_6^{3-}$ charge transfer. Acid shifts the charge-transfer band for Os(IV)–Fe(II) to higher energy, as does base (pH >10). We infer that in acid a proton is added to $Fe(CN)_6^{4-}$, raising the Fe(III)/Fe(II) redox potential; in base, coordinated water is deprotonated, thus lowering the Os(IV)/Os(III) redox potential, both processes increasing the energy barrier to electron transfer.

It has been shown[1] that *trans*-$[Os(en)_2(\eta^2\text{-}H_2)H_2O]^{2+}$ (**1**) in water readily undergoes substitution by a wide range of nucleophiles. Among them is $Fe(CN)_6^{4-}$, which differs from all others thus far reported[1,2] in that it readily undergoes $1e^-$ oxidation. While a dilute solution (slightly acidic) containing *trans*-$[Os(en)_2(\eta^2\text{-}H_2)Fe(CN)_6]^{2-}$ is colorless, on oxidation by $FeCp_2^+$ and other reagents a deep blue color develops, which we attribute to the formation of a mixed valence species. These properties were important in the characterization[3] of the product of oxidation of **1** by $FeCp_2^+$, and they led to this wider exploration of what we diagnosed as metal-to-metal charge-transfer absorption. The results we have obtained in studying the oxidation reaction, in characterizing the product, and in extending the investigation to $Ru(CN)_6^{4-}$, $Os(CN)_6^{4-}$, $Mo(CN)_8^{4-}$, and $Co(CN)_6^{3-}$ as nucleophiles form the basis of this report.

Glossary: **1** ≡ $[Os(en)_2(\eta^2\text{-}H_2)H_2O]^{2+}$ or the $CF_3SO_3^-$ salt; **2** ≡ $Os^{IV}(en)_2(H)(CF_3SO_3)_3{\cdot}CH_3OH$; $[Os(en)_2H]^{3+}$, presumed to be $[Os(en)_2H(H_2O)_2]^{3+}$ in H_2O; Os(II)–Fe(II) ≡ $[Os(en)_2(\eta^2\text{-}H_2)Fe(CN)_6]^{2-}$; Os(IV)–Fe(II) ≡ $[Os(en)_2(H)Fe(CN)_6]^-$; Os(IV)–Fe(III) ≡ $[Os(en)_2(H)Fe(CN)_6]$. A similar system is used for the $Co(CN)_6^{3-}$, $Ru(CN)_6^{4-}$, $Os(CN)_6^{4-}$, and $Mo(CN)_8^{4-}$ derivatives. Unless otherwise indicated, for all Os(II) species the amine ligands are in the trans arrangement. It is likely that all Os(IV) species here are heptacoordinated,[3] but H_2O is not always included in the formulas; water being the solvent, it is difficult to prove that it is bound to the metal center.

Experimental Section

Preparations. The preparations of **1** and **2** are described in refs 2 and 3, respectively.

(a) $\mathbf{K[Os(en)_2(H)(H_2O)Fe(CN)_6]}$**.** A solution (2 mL) was prepared containing each of **1** and $K_4Fe(CN)_6{\cdot}3H_2O$ at 0.033 M and HCF_3SO_3 at 0.010 M. The solution was bubbled with O_2 for 2 min, after which time there was no further change in the blue color which developed. On addition of C_2H_5OH, a blue precipitate formed; this was collected, washed with ethanol, and dried. Yield: 80%. Anal. Calcd: C, 20.68; H, 3.27; N, 24.13. Found: C, 20.34; H, 3.47; N, 23.62. Attempts to purify the compound by redissolution in water or methanol failed because we found that very little dissolves.

(b) $\mathbf{[FeCp_2]CF_3SO_3}$**.** A 30-mL ether solution of ferrocene (1 mM) was mixed with 30 mL of an ether solution of *p*-benzoquinone (2 mM) and trifluoromethanesulfonic acid (4 mM, 50% aqueous solution). The resulting blue precipitate was filtered off and washed thoroughly with ether. Anal. Calcd for $[Fe(C_5H_5)_2]CF_3SO_3$: C, 39.40; H, 2.99. Found: C, 39.35; H, 2.97.

Instrumentation. Ultraviolet–visible spectra were recorded with a Hewlett-Packard 8452A spectrophotometer. NMR spectra were obtained on a Varian XL-400 or Gemini 200 spectrometer. Infrared spectra were obtained on a Perkin-Elmer 1600 FTIR spectrophotometer. Electrochemical measurements were made under argon with a PAR Model 173 potentiostat driven by a PAR Model 175 universal programmer. Cyclic voltammagrams were recorded with a Pt° working electrode (1 mm²) and a Pt° counter electrode. A saturated calomel electrode (SCE) was used as the reference. The potentials were corrected to the normal hydrogen electrode (NHE) by adding 0.242 V to the measured values.

Results

I. Characterization of the Binuclear Complexes in Reduced Form.

When $Fe(CN)_6^{4-}$ is added to a solution of **1** in D_2O with each reagent at ca. 0.010 M, the ¹NMR signal characteristic of η^2-H_2 in the aquo form ($\delta = -13.45$ ppm) disappears and a new

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Table 1. ^{1}H NMR Data for Dihydrogen Complexes *trans*-$[Os^{II}(en)_2(\eta^2\text{–}H_2)Nu]^a$

Nu	$-\delta_{H_2}$ (ppm)	J_{H-D} (Hz)	$T_1(H_2)^b$ (ms)	$\delta_{NH_2}{}^c$ (ppm)	$\delta_{CH_2}{}^d$ (ppm)
$Fe(CN)_6{}^{4-}$	10.24	13.8	30	4.86; 4.02	2.50; 1.98
$Ru(CN)_6{}^{4-}$	10.16	14.0	59	4.87; 4.01	2.48; 1.98
$Os(CN)_6{}^{4-}$	10.13	15.3	52	4.84; 4.00	2.56; 2.01
$Co(CN)_6{}^{3-}$	9.94	15.7	72	4.93; 3.99	2.43; 2.04
$Mo(CN)_8{}^{4-}$	9.41, 9.45, 9.51	18.3	67	5.15; 4.02	2.54; 2.10
CH_3CN	9.13	17.9	79	5.34; 4.67	2.67; 2.34

[a] Values of $-\delta_{H_2}$ for cis forms are as follows, in the order of presentation in the table: 8.73, 8.60, 8.66, 8.26, 8.32 (broad), 7.64. [b] 200 MHz, 20 °C. [c] All singlets. [d] All multiplets.

signal appears at $\delta = -10.24$ ppm. The substitution reaction is quite rapid, and it is complete by the time the first measurements are made, ca. 5 min after mixing. Even at these concentrations, no trace of the ^{1}NMR peak for **1** is discernible at equilibrium. The affinity of $Fe(CN)_6{}^{4-}$ for **1** is apparently high, and we find no effects arising from dissociation of the complex in the manipulations we have carried out, except possibly when the reaction solution is strongly acidic, >0.10 M H^+. (It should be noted that K_{diss} for $HFe(CN)_6{}^{3-}$ is reported[4] as $(6.7 \pm 0.3) \times 10^{-5}$.) The statement applies also to the other cyano complexes except that with $Co(CN)_6{}^{3-}$, where replacement by some other nucleophiles was observed.

The ^{1}H NMR data for the five complexes are summarized in Table 1. In the light of our previous experience, we were astonished to observe a weak splitting of the ^{1}H NMR signal for η^2-H_2 for some of the cyano derivatives. The separation is barely discernible at 200 MHz but is obvious at 400 MHz. See Figure 1.

The absorption spectra for **1** and for Os(II)–Fe(II) are shown in Figure 2. To be noted is that neither species shows strong absorption at λ >400 nm. The most prominent features of the spectrum of **1** are the strong band at $\lambda_{max} = 204$ nm ($\epsilon = 1.6 \times 10^3$ M^{-1} cm^{-1}) and a succession of shoulders at lower energies. The strong band presumably corresponds to charge transfer from Os(II), but whether to π^* of H_2 or to other centers of positive charge, e.g., protons of coordinated amines, is not known.[5] In the spectrum of Os(II)–Fe(II), two strong bands appear at high energy, assignable to the two metal centers. Two bands at high energy are observed for $Fe(CN)_6{}^{4-}$ itself ($\lambda_{max} = 214$ nm, $\epsilon = 4.6 \times 10^3$ M^{-1} cm^{-1}; $\lambda_{max} = 238$ nm, $\epsilon = 5.5 \times 10^3$ M^{-1} cm^{-1}). The values of ϵ for Os(II)–Fe(II) are even higher in this energy region because Os(II) also contributes. The absorptions at high energy in general are greater than the sum of the separate contributions. The lower energy bands arising from the Os(II) center are masked by the shoulder of the band for $Fe(CN)_6{}^{4-}$ at $\lambda_{max} = 238$ nm. We draw particular attention to the band at $\lambda_{max} = 320$ nm ($\epsilon = 1.1 \times 10^3$ M^{-1} cm^{-1}) which also appears in the spectrum of a solution of $K_4Fe(CN)_6$ ($\lambda_{max} = 320$ nm, $\epsilon = 4.0 \times 10^2$ M^{-1} cm^{-1}). There is residual absorption for **1** in this region but no maximum. None of the binuclear species with $[Os(en)_2(\eta\text{-}H_2)]^{2+}$ has absorption at $\lambda > 450$ nm, which is the region of particular interest for the Os(IV) binuclear species.

The major features of the absorption spectra of **1**, of $[Os(en)_2H]^{3+}$, of the binuclear species in the reduced form, and of the nucleophiles we have dealt with are summarized in Table 2.

Cyclovoltammetric measurements were made in aqueous solution, but, because of fouling of the electrodes, not without difficulty, especially in the case of the binuclear complexes. The electrochemical behavior of **1** is similar in all respects to that reported for $[Os(NH_3)_5(\eta^2\text{-}H_2)]^{2+}$.[6] In 0.10 M acid, at the sweep rate of 100 mV s^{-1}, beginning at low potentials, a couple is observed at $E_{1/2} = 0.64$ V, when the reverse sweep is begun short of 0.90 V. This peak, as in the case of $[Os(NH_3)_5(\eta^2\text{-}H_2)]^{2+}$ ($E_{1/2} = 0.41$ V) is attributed to the $[Os(\eta^2\text{-}H_2)]^{3+/2+}$ couple. The peaks

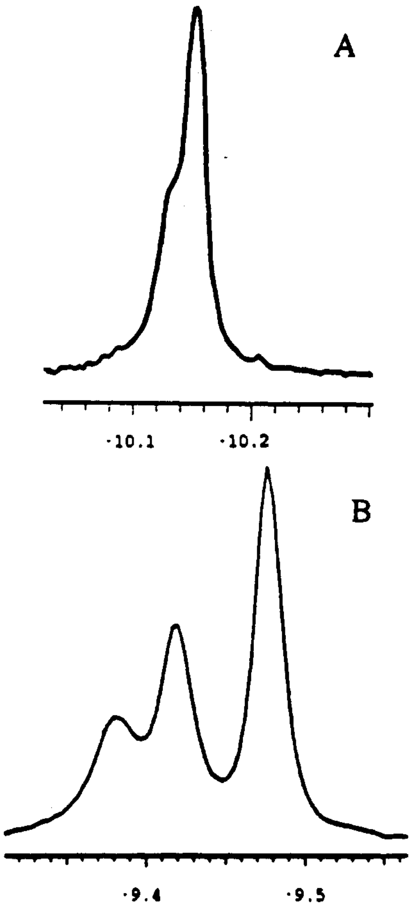

Figure 1. (A) The η^2-H_2 peak in the ^{1}H NMR spectrum (400 MHz) of $[Os^{II}(en)_2(\eta^2\text{-}H_2)Fe(CN)_6]^{2-}$ in D_2O. (B) The η^2-H_2 peak in the ^{1}H NMR spectrum (400 MHz) of $[Os^{II}(en)_2(\eta^2\text{-}H_2)Mo^{IV}(CN)_8]^{2-}$ in D_2O.

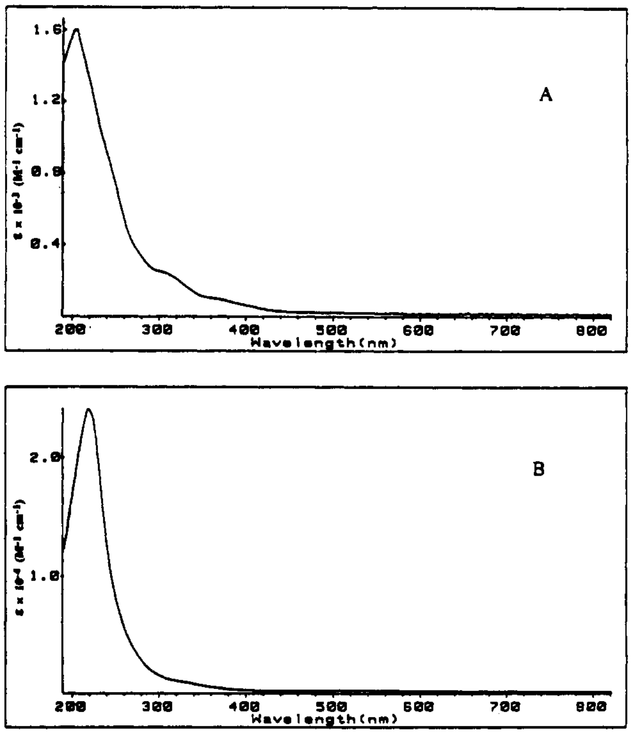

Figure 2. (A) Absorption spectrum of $[Os(en)_2(\eta^2\text{-}H_2)H_2O]^{2+}$ (1.1×10^{-3} M) in H_2O. (B) Absorption spectrum of $[Os^{II}(en)_2(\eta^2\text{-}H_2)Fe^{II}(CN)_6]^{2-}$ (9.5×10^{-5} M) in H_2O.

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(5) Theoretical analysis of the spectrum of this and related species is underway by N. S. Hush and co-workers, University of Sydney.

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(7) Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.*, in submission.

Table 2. Ultraviolet–Visible Data for Complexes **1** and **2** and for Cyanometalate Complexes[a]

complex	λ_{max} (nm) (ϵ_{max} (M^{-1} cm^{-1}))
$[(en)_2Os(H_2)]^{2+}$	204 (1.6×10^3); 240 (9.0×10^2); 278 (3.5×10^2); 308 (2.5×10^2); 370 (88)
$[(en)_2Os(H)]^{3+}$	200 (1.4×10^4); 220 (7.9×10^3); 288 (5.7×10^3); 314 (1.2×10^3)
$Fe(CN)_6^{4-}$	214 (4.6×10^3); 238 (5.5×10^3); 266 (2.4×10^3); 320 (4×10^2)
$Fe(CN)_6^{3-}$	210 (4.4×10^3); 262 (1.2×10^3); 284 (1.2×10^3) (sh); 304 (1.6×10^3); 320 (1.1×10^3); 400 sh (9.0×10^2); 420 (1.0×10^3)
$Ru(CN)_6^{4-}$	214 (3.3×10^3); 234 (3.7×10^3)
$Ru(CN)_6^{3-}$	214 (6.1×10^3); 226 (6.0×10^3); 252 (1.5×10^3); 300 (2.3×10^3); 330 (2.5×10^3); 356 (1.6×10^3); 472 (7.8×10^2)
$Os(CN)_6^{4-}$	192 (4.3×10^4);212 (4.7×10^4)
$Co(CN)_6^{3-}$	208 (3.5×10^3); 258 (1.6×10^2); 213 (2.0×10^2)
$Mo(CN)_8^{4-}$	196 (6.6×10^3); 238 (1.1×10^4); 278 (1.0×10^3)
$[(en)_2Os^{II}(H_2)Fe(CN)_6]^{2-}$	220 (2.4×10^4); 320 (1.1×10^3)
$[(en)_2Os^{II}(H_2)Ru(CN)_6]^{2-}$	212 (7.9×10^3); 234 (9.3×10^3); 294 (9.7×10^2)
$[(en)_2Os^{II}(H_2)Os(CN)_6]^{2-}$	212 (3.2×10^4)
$[(en)_2Os^{II}(H_2)Co(CN)_6]^{-}$	212 (7.5×10^3); 296 (7.6×10^2)
$[(en)_2Os^{II}(H_2)Mo(CN)_8]^{2-}$	210 (6.4×10^3); 238 (7.4×10^3); 260 (7.1×10^3); 360 (8.0×10^2); 424 (2.8×10^2)

[a] In aqueous solution, without added acid or base.

Table 3. Electrochemical Data[a]

complex[b]	$E_{1/2}$[c,d] (V)	medium
$[Os^{II}(en)_2(H_2)]^{2+}$	0.62	0.1 M CF_3SO_3H
$[Os^{IV}(en)_2H]^{3+}$	0.63	0.1 M CF_3SO_3H
$Fe(CN)_6^{4-}$	0.36[9]	
Os(IV)–Fe(II)	0.59	0.1 M CF_3SO_3H
	0.80	0.1 M CF_3SO_3H
$Ru(CN)_6^{4-}$	0.86[11]	
Os(IV)–Ru(II)	0.76	1.0 M CF_3SO_3H
$Os(CN)_6^{4-}$	0.63[10]	
Os(IV)–Os(II)	0.62	0.1 M CF_3SO_3H
Os(IV)–Co(III)	0.57	0.1 M CF_3SO_3H
$Mo(CN)_8^{4-}$	0.73[12]	
Os(IV)–Mo(IV)	0.71	0.1 M CF_3SO_3H

[a] All in aqueous 0.10 M CF_3SO_3H except for Os(IV)–Ru(II) at 1.0 M CF_3SO_3H. [b] All oxidized by $S_2O_8^{2-}$, except $[(en)_2Os^{IV}H]$, which is oxidized by Ce^{IV}. [c] Vs NHE. [d] All exhibit an oxidation current above 0.9 V, but a well-developed maximum is yielded only in the case of Os(IV)–Fe(II).

are broad, and the peak to peak separation is large, 0.22 V. When the oxidation sweep is carried beyond 0.9 V, a second oxidation wave is observed, which is of greater amplitude and, as in the case of $[Os(NH_3)_5(\eta^2\text{-}H_2)]^{2+}$, is ascribable to the electrode reaction $[Os^{III}(H_2)] \rightarrow Os(III) + 2H^+ + 2e^-$. Similar behavior at high potentials is observed also for the other binuclear complexes. For each of Os(II)–Co(III), Os(II)–Ru(II), and Os(II)–Mo(IV), a single value of $E_{1/2}$ is registered when the reverse sweep is started at a potential just short of the onset of the final oxidation wave, while, in the case of Os(II)–Fe(II), two values of $E_{1/2}$ are registered in this range. For the last mentioned, there was a complication in that, in the sweep to higher potential, an oxidation wave appears before reaching the potential at which the first value of $E_{1/2}$ is observed. It is of variable amplitude and is small, and in no case is it as large as that expected for a $1e^-$ change. We attribute it to the formation of a coating on the electrode. In some cases, notably for Os(II)–Ru(II), very high currents are registered in the voltage range where the $2e^-$ oxidation wave is expected. The results of the electrochemical measurements are summarized in Table 3. Included are those obtained with compound **2** and those obtained by using a sample of Os(II)–Fe(II) which had undergone $2e^-$ chemical oxidation ($S_2O_8^{2-}$, Ce(IV)) before the measurements were made. It should be noted that for each of the oxidized products, the electrochemical features observed agree rather well with those obtained when the respective reduced forms are used. Additionally, we found that rather cleaner electrochemical behavior was observed when the oxidized form was used. A trace for this kind of experiment starting with Os(IV)–Fe(II) is shown in Figure 3. Included in the solution as an internal standard was $Ru(NH_3)_6^{3+/2+}$ at the same concentration as that of Os(IV)–Fe(II). The relative amplitudes suggest that each of the two couples recorded for the binuclear complex corresponds to a $1e^-$ change. That this is indeed the case was shown more rigorously by use of rotating-disk polarography. In the experiment starting with Os(IV)–Fe(II), the spurious oxidation peak we observed with Os(II)–Fe(II) was absent. However a good electrochemical response such as is shown in Figure 3 was observed only for the first cycle. The observations outlined were made with a platinum electrode. Similar behavior was noted with glassy carbon as electrode material, but gold was not found to be suitable.

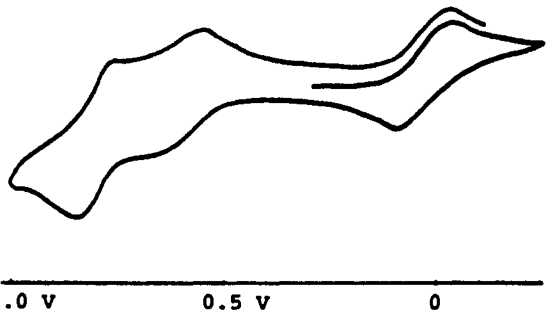

Figure 3. Cyclic voltammogram of $[Os^{IV}(en)_2(H)Fe^{II}(CN)_6]^-$ (5.4×10^{-3} M in H_2O, 0.1 M CF_3SO_3H, 6.6×10^{-3} M $[Ru(NH_3)_6]^{3+}$ added as standard gives the signal at 0.0 V at ca. 100 mV/s; potentials vs NHE).

A number of experiments were done to reduce $[Os(en)_2H]^{3+}$ by other than electrochemical means. Reduction by Zn/Hg is efficient: a solution of **1**, 4.0×10^{-3} M, in 1.0 M DO_3SCF_3 in D_2O, was oxidized by the required amount of $[Cp_2Fe]O_3SCF_3$, Cp_2Fe was removed by filtration, Zn/Hg was added to the solution (1.0 g in 10 mL) and the mixture was stirred. Reaction was found to be complete in 5 min; the final yield, as determined by ^1H NMR signals of the protons of $NH_2C_2H_4NH_2$, was found to be 80% of theoretical. However, with the homogeneous reducing agents ascorbic acid, $[Ru(NH_3)_5H_2O]^{2+}$, $Ru(NH_3)_6^{2+}$, and $SnCl_2$, at 0.50, 0.080, 0.050, and 0.1 M, respectively (0.10 M HO_3SCF_3), there was less than 2% formation of **1** even after 24 h.

Because of the intense color of Os(IV)–Fe(II), its reduction is easy to follow. In contrast to facile reduction of $[Os(en)_2H]^{2+}$ by Zn/Hg, even after exposure of Os(IV)–Fe(II) to the reductant for 2 days, very little change in the intensity of the blue color was observed.

Our conclusion that the affinity of **1** for $Fe(CN)_6^{4-}$ is very high is supported by experiments with **1** in excess of $Fe(CN)_6^{4-}$. With **1** at 0.023 M and $Fe(CN)_6^{4-}$ at 1.20×10^{-3} M, by taking account of the relative intensities of the ^1H NMR signals at the positions characteristic of **1** when it is bound to $Fe(CN)_6^{4-}$ and when it is free, we calculate that 5.8 molecules of **1** are bound for each $Fe(CN)_6^{4-}$. The accumulation of **1** on $Fe(CN)_6^{4-}$ does not change δ (η^2-H_2) noticeably, but the signal is broadened, showing some structure. The ^1H NMR signals for the amines in the two environments—$[Os(en)_2H_2]^{2+}$ coordinated to H_2O and to

$Fe(CN)_6^{4-}$ —are well enough resolved, and their use confirms that more than five molecules of **1** are ligated to one $Fe(CN)_6^{4-}$.

II. Characterization of Oxidation Products. In an earlier publication[3] evidence was cited supporting the conclusion that the product of the $2e^-$ oxidation of **1** contains as the core $[Os(en)_2(H)]^{3+}$ and that two additional coordination sites are occupied. We assume that, in the absence of a better nucleophile, two molecules of water are attached.

In the description of the binuclear complexes, the observations made on oxidizing Os(II)–Fe(II) and on characterizing the product will be dealt with first, because this system was the most thoroughly investigated.

In view of the fact that $E_{1/2}$ for the first stage of oxidation is at 0.64 V, it was a surprise to learn that Os(II)–Fe(II) is very sensitive to air. If the solution is acidic, a blue color is seen to develop in the colorless solution immediately on exposure to air (in the absence of acid, the product has a rose color). The reaction stoichiometry was established by a series of experiments in which a solution saturated with O_2 (1.1×10^{-3} M) was mixed with a solution of Os(II)–Fe(II) at the same concentration, each solution being acidified (0.10 M CF_3SO_3). Reaction was complete by the time the optical densities were read, ca. 2 min. The extinction coefficients measured at the band maximum, 592 nm, for the product at $[O_2]/[Os(II)–Fe(II)]$ ratios of 0.50, 1.00, and 5.00 were 0.88×10^2, 1.77×10^3, and 1.81×10^3 M^{-1} cm^{-1}, respectively. When $S_2O_8^{2-}$ was used as oxidant, in a similar procedure, the general behavior was as described for O_2; that is, a limiting extinction coefficient was reached at a 1:1 mole ratio, but the extinction coefficient measured is somewhat below that recorded when O_2 is oxidant. As already reported, when $FeCp_2^+$ is oxidant, we find that the full development of the blue color involves a $2e^-$ change, and we thus conclude that H_2O_2 is the first reduction product when O_2 is oxidant. We have found that H_2O_2 reacts only extremely slowly with the colored product.

Oxidation to the colored product, as might be expected, is rapid also with Ce(IV), but with this strong oxidant, as can be the case also with $S_2O_8^{2-}$, production of the blue product is not quantitative when the reaction is carried to the theoretical end point. This is not surprising because, toward the end of the titration, the concentration of Os(II)–Fe(II) is small compared to that of the blue product, which in the case of $S_2O_8^{2-}$ may be susceptible to attack by radical intermediates, even if not by the oxidant.

That not both metal centers are involved in the overall net $2e^-$ change is indicated by the fact that there is no intermediate stage in the oxidation: to wit, the spectrum of the colored product when half the binuclear complex is oxidized is identical to that observed when it is fully oxidized. Even more convincing is the following evidence. Hexacyanoferrate(II) has an absorption band at 320 nm which appears also in the spectrum of Os(II)–Fe(II), and its position is unaltered during the oxidation, though there are increases in intensity owing to a contribution by $[Os(en)_2H]^{3+}$. In the wavelength region 400–450 nm, where the absorption for the colored product is low, $Fe(CN)_6^{3-}$ absorbs strongly (420 nm, $\epsilon = 1.0 \times 10^3$ M^{-1} cm^{-1}) and there is no hint of a band maximum at this wavelength in the spectrum of the colored product, shown in Figure 4A. Bands characteristic of $Fe(CN)_6^{3-}$ do develop when Ce(IV) is added to a solution containing the Os(IV)–Fe(II) species.

Finally we note that the IR spectrum of the solid product (described under Preparations) shows the C≡N stretch at 2046 cm^{-1}, close to that for $K_4Fe(CN)_6$ (2033 cm^{-1}) and well removed from that for $K_3Fe(CN)_6$ (2122 cm^{-1}).

The fact that the osmium center in Os(II)–Fe(II) undergoes a net $2e^-$ change, as does **1**, taken together with the fact that the electrochemical behavior of the blue product is similar to that of Os(II)–Fe(II), supports the formulation we have adopted for the blue species. It is to be noted as well that a blue product with absorption characteristics identical to those described above under similar circumstances is formed almost quantitatively when solutions of $[Os(en)_2H]^{3+}$ and of $K_4Fe(CN)_6$ are mixed in a 1:1 ratio.

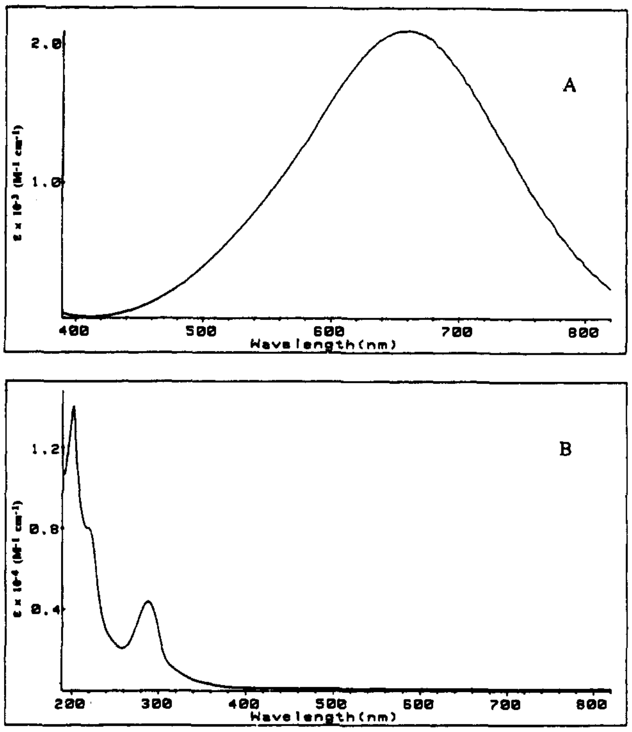

Figure 4. (A) Absorption spectrum (in visible region) of $[Os^{IV}(en)_2(H)Fe^{II}(CN)_6]^-$ (4.2×10^{-4} M) in H_2O. (B) Absorption spectrum of $[Os^{IV}(en)_2(H)]^{3+}$ (1.4×10^{-4} M) in H_2O.

Because in the application of cyclic voltammetry to **1** a reversible $1e^-$ couple in acidic solution is identified, implying at least a fleeting existence of Os(III)–(η^2-H_2), we undertook to learn whether, in mixtures of **1** and $[Os(en)_2H]^{3+}$, a detectable concentration of such a species is built up. The earlier electrochemical observations[6] showed that while Os(III)–(η^2-H_2) remains intact in acidic solution (cyclic voltammetry time scale), it disappears rapidly in an unacidified medium, by deprotonation, possibly followed by disproportionation. When the oxidation state of the metal is increased to 4+, it is expected that the affinity of coordinated hydride for the proton will decrease, so that even in quite acidic solution the disproportionation equilibrium would be representable by the equation

$$2[Os(en)_2(\eta^2\text{-}H_2)(H_2O)]^{3+} + H_2O = [Os(en)_2(\eta^2\text{-}H_2)(H_2O)]^{2+} + [Os(en)_2(H)(H_2O)_2]^{3+} + H^+ \quad (1)$$

i.e., increasing the concentration of acid will favor the formation of the intermediate oxidation state. Accordingly, a series of solutions of varying acidity were prepared in which equal concentrations of **1** and $[Os(en)_2H]^{3+}$ were mixed, at concentrations of HCF_3SO_3 in the range 0.10–8.0M, and the absorption spectra of the mixtures were compared with the sums of the spectra for the separate components at the same acidity. In each case, the spectra were additive even at highest acid concentrations.

In early experiments on the oxidation of Os(II)–Fe(II) in initially neutral solution, it was noted that while the product with $S_2O_8^{2-}$ as oxidant is blue, when O_2 is oxidant it is rose colored. This difference was traced to a difference in stoichiometry. Oxygen

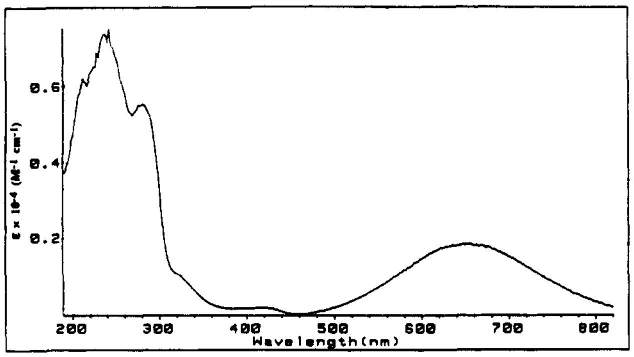

Figure 5. Absorption spectrum of $[Os^{IV}(en)_2(H)Fe^{III}(CN)_6]$ (4.6×10^{-4} M) in H_2O.

in acting as an oxidant requires protons

$$[Os(en)_2(\eta^2\text{-}H_2)(H_2O)]^{2+} + O_2 + H_2O = [Os(en)_2(H)(H_2O)OH]^{2+} + H_2O_2 \quad (2)$$

while $S_2O_8^{2-}$ does not. Oxidation of **1** by $S_2O_8^{2-}$ in fact produces acid

$$[Os(en)_2(\eta^2\text{-}H_2)H_2O]^{2+} + S_2O_8^{2-} + H_2O = [Os(en)_2(H)(H_2O)_2]^{3+} + 2SO_4^{2-} + H^+ \quad (3)$$

The rose-colored product turns blue on the addition of a small amount of acid. A solution of the blue form was prepared by oxidation with $S_2O_8^{2-}$, and on measurement of the pH after oxidation, it was found to be that expected according to eq 2. Upon the addition of NaOH, a new band at higher energy develops, and in 0.010 M NaOH, two maxima are observed, at 556 nm ($\epsilon = 1.1 \times 10^3$ M^{-1} cm^{-1}) and at 660 nm, the original wavelength, but ϵ now is reduced to 9.8×10^2 M^{-1} cm^{-1} compared to 2.1×10^3 M^{-1} cm^{-1} as in Figure 4. The titration was not carried further because there is evidence of decomposition in alkaline solution. This was still minor because, on reacidification, the spectrum reverts to that shown in Figure 4, with ϵ somewhat reduced (1.8×10^3 M^{-1} cm^{-1}).

The color changes from blue to rose also in acidic solution. For Os(IV)–Fe(II) a limiting spectrum for the acidic form is reached in 1 M HCF_3SO_3 with $\lambda_{max} = 540$ nm ($\epsilon = 1.4 \times 10^3$ M^{-1} cm^{-1}). By measuring the absorbances of solutions (0.100–0.050 M H^+) in which both limiting forms are present at comparable concentrations and taking into account the absorbances of the limiting forms, we measured the pK_a for the acid form as 1.2 ± 0.3. This is an approximate value because no effort was made to control ionic strength.

Elsewhere,[3] the growth in the absorbance of Os(IV)–Fe(II) as the concentration of $Fe(CN)_6^{4-}$ is increased was reported, and the effect was attributed to the formation of a diiron(II) complex, in line with the conclusion that the coordination number of Os(IV) with the ligands dealt with in the study is 7. Changes in the absorption of Os(IV)–Fe(II) are brought about also by other nucleophiles. The experiments were done on separate portions of a solution, each containing Os(IV)–Fe(II) at 9.9×10^{-4} M, which had been generated by the action of O_2 on a slightly acidic solution of **1**. The pH of the solution at this stage was 4; $\lambda_{max} = 642$ nm; $\epsilon = 2.4 \times 10^3$ M^{-1} cm^{-1}. Upon the addition of SO_4^{2-} to raise its concentration to 1.2×10^{-2} M, there was no immediate response except a shift of λ_{max} to 646 nm. But after 1 h, λ_{max} changed to 660 nm and ϵ was measured as 3.1×10^3 M^{-1} cm^{-1}. On addition of Cl^- (1.2×10^{-2} M), there was a rapid shift of the maximum to 650 nm, ϵ rising by 10%, and after 1 h, λ_{max} was measured at 660 nm ($\epsilon = 3.2 \times 10^3$ M^{-1} cm^{-1}).

While the products of the oxidation by O_2, $S_2O_8^{2-}$, and $FeCp_2^+$ are similar, they are not identical. In the preparation of the solutions of Os(IV)–Fe(II) with O_2, the oxidant was in excess at the end of the reaction, but to minimize overoxidation with the more powerful agent $S_2O_8^{2-}$, it was the limiting reagent. In the later stages of the work, after we had succeeded in preparing $[FeCp_2]CF_3SO_3$, which, in contrast to $[FeCp_2]PF_6$, is water soluble, this was also used as oxidant and again as the limiting reagent. For solutions at pH 3, where protonation of bound $Fe(CN)_6^{4-}$ is small, the characteristics (λ_{max}, nm (ϵ, M^{-1} cm^{-1})) observed are as follows: O_2, 644 (1.8×10^3); $S_2O_8^{2-}$, 662 (2.1×10^3); $FeCp_2^+$, 658 (2.1×10^3). The difference in extinction coefficient between O_2 and the others is not significant, but the difference in the wavelength of the maximum is considered to be real.

As much as possible, the observations on the absorption spectrum of Os(IV)–Fe(II) were made promptly after its formation. This is readily done when the species is generated from Os(II)–Fe(II) by oxidation, because the oxidation phase is over in less than 5 min with either $S_2O_8^{2-}$ or $FeCp_2^+$. When a solution prepared in this manner is stored, the extinction coefficient rises slowly and there is also a small bathochromic shift in the band maximum. An experiment was done by mixing a solution of **1** (final concentration 5.8×10^{-4} M) with one containing $Fe(CN)_6^{4-}$, this in 5% excess. It was oxidized by 2 equiv of $FeCp_2^+$, and the change in absorption was followed as a function of time. Just after completion of the oxidation phase, λ_{max} for Os(IV)–Fe(II) was registered at 658 nm ($\epsilon = 2.1 \times 10^3$ M^{-1} cm^{-1}). After 20 h, λ_{max} had shifted to 666 nm and ϵ had increased to 3.1×10^3 M^{-1} cm^{-1}, and after several days, it had risen to 4.0×10^3 M^{-1} cm^{-1}. The "aging" effect is not the cause of the increase in ϵ noted when SO_4^{2-} or Cl^- is added at high concentration. The response to this concentration perturbation is much more rapid than the aging under discussion. Moreover, it will be noted that ϵ for the solutions used as reference was 2.4×10^3 M^{-1} cm^{-1}, so that the aging in them had already progressed rather far before the anions were added. The reaction leading to the increase in absorption on aging does not obey first-order kinetics, and the apparent half-life increases with time, in line with a reaction order higher than first.

When $[Os(en)_2H]^{3+}$ is in excess of $Fe(CN)_6^{4-}$, species are formed in which it clusters about $Fe(CN)_6^{4-}$. A solution was prepared 6.6×10^{-4} M in **1** and 2.8×10^{-4} M in $Fe(CN)_6^{4-}$ and enough $FeCp_2^+$ was added to convert **1** to $[Os(en)_2H]^{3+}$. The band in the visible region which for Os(IV)–Fe(II) appears at 664 nm ($\epsilon = 2.1 \times 10^3$ M^{-1} cm^{-1}) now appears at 632 nm (ϵ calculated per $Fe(CN)_6^{4-}$ now is 4.2×10^3 M^{-1} cm^{-1}). With **1** at 1.12×10^{-3} M and $Fe(CN)_6^{4-}$ at 1.65×10^{-4} M, $\lambda_{max} = 598$ nm and $\epsilon = 6.1 \times 10^3$ M^{-1} cm^{-1}.

Though the Os(IV) complexes formed from the other cyano complexes were not studied in the same depth as was Os(IV)–Fe(II), we have in addition to comparisons of electrochemical properties, already introduced, data on the absorption spectra in the visible region. These data are summarized in Table 4. Included also are the data for $[Os(en)_2H]^{3+}$ produced by the action of $FeCp_2^+$ on **1**. See also Figure 4B.

Preliminary experiments were also done with $Fe(CN)_6^{3-}$ as nucleophile. In our first attempts, Os(IV)–Fe(II) was prepared as already described and an equivalent amount of Ce(IV) was added. Reaction is rapid, leaving the resulting solution blue. The formation of $Fe(CN)_6^{3-}$ is indicated by the appearance of a new absorption at ~420 nm. However, at most, 80% of the $Fe(CN)_6^{4-}$ is oxidized. The product spectrum has a number of features which are difficult to account for, and we infer that, in addition to the desired process, oxidation at the osmium center takes place. Simpler behavior is observed when a solution of $[Os(en)_2H]^{3+}$ prepared by oxidizing **1** with $FeCp_2^+$ is mixed with one containing $Fe(CN)_6^{3-}$, the reagents being present in equal concentrations. Substitution, particularly in the last stages when the reagents are depleted, is slow. In Figure 5 is shown the absorption spectrum

Table 4. Absorption Characteristics of the 1:1 Adducts of Osmium(IV) Monohydride with Cyano Complexes^a

nucleophile	λ_{max} (nm) ($10^{-3}\epsilon$ (M^{-1} cm^{-1}))	acidity
$Fe(CN)_6^{4-}$	556 (1.4)	1.0 M H^+ ^{b}
	662 (2.1)	pH 3.0
	678 (0.96); 556 (1.1)	Ph 12.0^c
	556 (1.2)^f	1.0 M H^+
	666 (2.1)^f	pH 12.0^c
	550 (1.2); 670 (0.8)^f	pH 12
$Fe(CN)_6^{3-}$ ^{f}	654 (2.3)	pH 7
$Ru(CN)_6^{4-}$	466 (1.4)	1.0 M H^+
	516 (2.1)	pH 3
	524 (1.0); 456 (1.1)	pH 12.0^c
$Os(CN)_6^{4-}$ ^{e}	4.98 (2.3)	1.0 M H^+ ^{b}
	592 (2.2); 512 sh (1.8)^d	pH 3
$Co(CN)_6^{3-}$ ^{e}	514 (0.21); 380 (3.0)^f	0.10 M H^+
	504 (0.27); 378 (3.0)^g	0.10 M H^+
$Mo(CN)_8^{4-}$	684 (1.7)	0.10 M H^+
	696 (1.7)	0.10 M H^+
	702 (2.3)	pH 7

^{a} Prepared from Os(II) adducts by oxidation with $S_2O_8^{2-}$ unless otherwise noted. ^{b} HCF_3SO_3 for all acidic conditions. ^{c} NaOH. ^{d} We had difficulty in preparing a good sample of $Os(CN)_6^{4-}$ and are inclined to ascribe the shoulder to an impurity. ^{e} Absorption independent of acidity, pH 1.0 to neutral. ^{f} $[FeCp_2]CF_3SO_3$ as oxidant. ^{g} Ce(IV) as the nitrato complex as oxidant.

obtained 2 min after mixing. The characteristics are remarkably similar to those observed for $Fe(CN)_6^{4-}$ as nucleophile. The Os(IV)–Fe(III) species show changes on aging similar to those described for Os(IV)–Fe(II). The band maximum soon after mixing appears at 654 nm ($\epsilon = 1.2 \times 10^3$ M^{-1} cm^{-1}). After 1 day, it shifts to 660 nm and ϵ rises to 3.4×10^3 M^{-1} cm^{-1}.

When an aqueous solution of Os(II)–Fe(II) is kept for more than a few hours, new ^1H NMR peaks appear at the expense of the parent peak. The splitting pattern for the CH_2 and NH_2 protons show that the new complex has the cis configuration. Reaction appears to be complete in 1 day, and by comparing the intensity of the new peak at −8.73 ppm with that of the parent peak at −13.8 ppm, we calculate the ratio of trans to cis at equilibrium to be ca. 3:1. This ratio does not change significantly even after the solution is heated at 70–80 °C for 2 h. A small splitting of the peak at −8.73 ppm is observed, just as is the case for the trans form. On oxidation to the Os(IV)–Fe(II) form, no dramatic differences in the absorption spectrum in the visible region are observed, as compared to that of a solution containing only *trans*-Os(IV)–Fe(II). The observations in the same regard, made with the nucleophiles $Ru(CN)_6^{4-}$, $Os(CN)_6^{4-}$, $Co(CN)_3^{3-}$ and $Mo(CN)_8^{4-}$, are similar except that, in the case of $Mo(CN)_8^{4-}$, the ratio of trans to cis at equilibrium is 5:1. The values of δ (ppm) for the cis forms were measured as −8.60, −8.66, −8.26, and −8.32 respectively. The signal for η^2-H_2 in the last case is broad and unsymmetrical, suggesting a coalescence of peaks.

At the time we first prepared $K[Os(en)_2(H)(H_2O)Fe(CN)_6]$, it was not clear whether the failure of the compound to dissolve in water was a matter of irreversible changes in the solid or of inherently low solubility. While there may be irreversible changes in the solid state, a series of episodes to be described show that at least some of the solutions we have been working with are supersaturated. Routinely, reaction mixtures are prepared in unused ampules and then dispensed into spectrophotometric cells for measurement. Quite late in the research we are reporting, and to our surprise, we found that though solutions in the ampules remained clear, on distribution to the spectrophotometric cells, precipitation would occur, the supernatant liquid, initially a deep blue, becoming almost colorless. When the cells were cleaned with warm nitric acid, metastability was restored and failures due to precipitation became infrequent. It is remarkable that solutions have been kept for weeks without a solid phase separating.

Discussion

Species in the Reduced State. In the discussion of the experimental results, an effort will be made to follow the order of their presentation in the previous section. A point of interest in the ^1H NMR results shown in Table 1 is that the similarity in the values of the properties includes CH_3CN as ligand. The value of δ and J_{H-D} in particular suggest that the electronic effects at the Os center attributable to the modification of $C{\equiv}N^-$ by the addition of CH_3^+ to the carbon are similar to those—to take an example—of $Fe(CN)_5^{3-}$ adding to CN^-. Whatever these similarities are, they do not dominate in determining the affinities of the nitriles for the site on Os(II) trans to η^2-H_2. The association quotient for the formation of Os(II)–Fe(II) is estimated as exceeding 10^5; that for $Co(CN)_6^{3-}$ is considerably lower—in an acetate buffer medium, we have observed replacement of $Co(CN)_6^{3-}$ but not of $Fe(CN)_6^{4-}$. For CH_3CN, the association quotient has been determined[7] as 2.6×10^2 at 25 °C. While the back-bonding capacity of Os(II) is very great, it appears to be much reduced in **1** because η^2-H_2 acts as a π acid, and the comparison of affinities suggests that electrostatic effects contribute significantly to the differences in affinities.

A second point of interest in the ^1H NMR observations is the splitting of the ^1H NMR signal for η^2-H_2 (see Figure 1). This may be a result of the isomer possibilities arising from the mutual arrangement of the δ,λ conformers of the ethylenediamines. The nucleophiles featured in the present work are the bulkiest of those thus far studied, and the crowding may impede the interconversion of the conformers. On this basis, two signals are expected for the hexacyano complexes, but for $Mo(CN)_8^{4-}$, if the coordinated ion is dodecahedral as it is in some salts[8] four can result, the doubling of the possibilities compared to the octahedron arising from the two kinds of donor sites offered by the dodecahedral geometry.

The point has already been made that the behavior of the hydridoosmium(IV) species in cyclic voltammetry is very much like that of the related Os(II)–(η^2-H_2) form. At an electrode, with a suitable surface, reduction of the former to the latter is rapid—though this proved not to be the case for the two homogeneous reducing agents we tested. It will be noted however that the values of $E_{1/2}$ registered for the first two entries in the table are not identical. Because of the difficulties we have had with the electrochemical measurements, already referred to, no significance can be attached to the difference. While it is true that **2** contains coordinated CH_3OH and that its replacement from **2** is known to be slow,[3] on reduction to **1**, we expect it to be replaced rapidly by H_2O, so that identical electrochemical behavior is expected in ordinary circumstances.

In the case of Os(II)–Fe(II), because both metal centers are electroactive at potentials below that at which the $2e^-$ oxidation wave is observed, the assignment of the two values of $E_{1/2}$ observed is not immediately obvious. The value of E° for $Fe(CN)_6^{3-/4-}$ is reported[9] as 0.36 V, and at first sight this would suggest that the lower of the two values of $E_{1/2}$ should be assigned to this couple. However the value of E_f, the formal potential registered at equal concentrations of oxidant and reductant, is raised by tenths of a volt even by cations such as Na^+ or K^+, and especially by H^+. Association with a tripositive ion is expected to have a very large effect of this kind. As a case in point, the wave corresponding to the oxidation of coordinated $Os(CN)_6^{4-}$ ($E° = 0.63$ V)[10] does not appear before the onset at ~1.0 V of the wave corresponding to oxidation of Os(III)–H_2. (For $Ru(CN)_6^{4-}$, $E° = 0.86 \pm 0.05$ V,[11] and for $Mo(CN)_8^{4-}$, $E° = 0.73$ V[12]; the response

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(12) Malik, W. V.; Ali, I. *Indian J. Chem.* **1963**, *1*, 374.

for their oxidation as ligands on $[Os(en)_2(\eta^2\text{-}H_2)]^{2+}$ is similarly masked.) In most cases at high potentials (>1.0 V), a well-defined wave corresponding to a stoichiometric current is swamped by that arising from extraneous oxidations. Taking into account the bias introduced by ligation to a tripositive ion, we conclude that, for Os(II)–Fe(II), $E_{1/2}$ = 0.59 V is assignable to the $[Os(III)\text{–}H_2]/[Os(II)\text{–}H_2]$ couple and $E_{1/2}$ = 0.80 V is assignable to the $[Fe(CN)_6]^{3-/4-}$ couple. If these assignments are accepted, the values of $E_{1/2}$ for the $[Os(III)\text{–}H_2]/[Os(II)\text{–}H_2]$ couple when the osmium center is coordinated to $Fe(CN)_6^{4-}$, $Os(CN)_6^{4-}$, and $Ru(CN)_6^{4-}$ are 0.59, 0.63, and 0.76 V, respectively, the corresponding values of E° for the $M(CN)_6^{3-/4-}$ couples being 0.36, 0.63, and 0.86 V. Such a marked change in the value of $E_{1/2}$ for a common process, namely the 1e⁻ oxidation of $[Os^{II}(en)_2(\eta^2\text{-}H_2)L]$, for a series of substituents L which are so similar in composition suggests that there is rather strong electronic coupling in at least one of the two oxidation states of the osmium center. There is no evidence of strong electronic coupling of $Os^{II}\text{–}(\eta^2\text{-}H_2)$ to the nucleophiles, and thus the sensitivity of $E_{1/2}$ for the $[Os(III)\text{–}H_2]/[Os(II)\text{–}H_2]$ couple to E° for the cyano couples implies that the $[Os^{III}(H_2)M^{II}(CN)_6]$ species are delocalized, the electronic coupling leading to stabilization of $Os(III)\text{–}H_2$ by charge transfer from the cyano complex. This effect would be greatest for $Fe(CN)_6^{4-}$ because it is the strongest reducing agent of the three. Such delocalization would also contribute to the large increase in $E_{1/2}$ of the $Fe(CN)_6^{3-/4-}$ couple on coordination to the osmium center because this stabilization, involving Fe(II) → Os(III) charge transfer, is lost when the iron-containing center is oxidized. The absorption characteristics of the fleeting $[Os^{III}(en)_2(\eta^2\text{-}H_2)Fe^{II}(CN)_6)]$ species in the long-wavelength region of the spectrum would be of great interest, as providing evidence on the extent of delocalization.

While the data for $Mo(CN)_8^{4-}$ (E° = 0.73 V) fit in with the correlation under discussion, they do not materially strengthen it because other differences introduced by changing to an octacoordinated cyano complex may be operative. Because any change in oxidation state for $Co(CN)_6^{3-}$ is at least 1 V removed from the range under consideration, it would serve as a useful "blank" for other hexacyano complexes, were it not for the fact that the ionic charge is now different. As it is, the only meaningful comparison involving it that can be made is to note the effect on the $[Os(en)_2(\eta^2\text{-}H_2)]^{3+/2+}$ redox potential. As expected, the anion stabilizes Os(III) relative to Os(II). The change in potential however is surprisingly small; $E_{1/2}$ = 0.62 V vs 0.57 V.

Binuclear Species Containing Os(IV). We consider first the origin of the strong absorption in the visible region of the spectra recorded for $Fe(CN)_6^{4-}$ and also for the nucleophiles $Ru(CN)_6^{4-}$, $Os(CN)_6^{4-}$, and $Mo(CN)_8^{4-}$. The high intensity, $\epsilon \sim 2 \times 10^3$ M⁻¹ cm⁻¹, coupled with the fact that the nucleophiles all are rather readily oxidized by 1e⁻ changes, suggests that the bands arise from light-activated charge transfer from the reducing agents to the Os(IV) center.

It seems certain that the systems with the nucleophiles listed are valence localized. The energies corresponding to the transitions are all considerably higher than expected if only the Franck–Condon barrier to charge transfer contributes, and thus the difference in E° of the two sites, ΔE°, is an important factor in determining the energies.[13] Because of similarity in structure, the Franck–Condon barriers for 1e⁻ oxidation of $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, and $Os(CN)_6^{4-}$ will be nearly the same, and because the energies of the transitions for the three species differ considerably, ΔE° makes an important contribution to the energies of the transitions. ΔE° is least for $Fe(CN)_6^{4-}$ because, in this case, the transition is at the lowest energy. The bandwidth at half-height for this system is 0.50×10^4 cm⁻¹; that calculated from the relation[13] $\upsilon_{max} = (\upsilon_{1/2})^2/2310$, applicable to localized systems when $\Delta E^\circ = 0$, is 0.59×10^4 cm⁻¹. Were ΔE° for the two centers zero, this narrowing of the band would indicate a considerable degree of delocalization (for a number of compositionally symmetric mixed-valence molecules, the experimental half-width is ca. 1.2 times calculated from the equation above).[14] However, because ΔE° is unknown and so has not been allowed for in calculating the theoretical bandwidth, this easily accounts for the apparent narrowing. That this is indeed the case is indicated by the fact that, for Os(IV)–Ru(II), where the value of ΔE° will be greater than that for Os(IV)–Fe(II), the "band narrowing" is found to be even greater.

If, as is assumed, the Franck–Condon barriers for $Fe(CN)_6^{4-}$ and $Ru(CN)_6^{4-}$ are nearly the same, then the difference in the energies of the intervalence bands for them measures the difference in the redox potentials for the two cyano complexes. The difference in λ_{max} for $Fe(CN)_6^{4-}$, 660 nm, and λ_{max} for $Ru(CN)_6^{4-}$, 552 nm, is 0.47 V. The difference in E° for the two couples is 0.50 V. While it is true that values of E° are biased when a hexacyano complex coordinates to a tripositive ion, there is no obvious reason that the bias should be different for the two nucleophiles, at least if, as seems to be the case, the systems are localized. In such cases, stabilization of the ground state by delocalization is small, usually amounting to less than 2 kcal.

The intervalence band for Os(IV)–Os(II) lies between those observed for the congener complexes, and the value of E° for $Os(CN)_6^{3-/4-}$ is bracketed by those of the other two couples. However, even though E° for $Mo(CN)_8^{3-/4-}$ is 0.20 V higher than that for $Fe(CN)_6^{3-/4-}$, λ_{max} for the intervalence band at 700 nm is the lowest of those measured. On the basis of the arguments presented, the result implies a much smaller Franck–Condon barrier to electron transfer for the octacyano complex compared to the hexacyano, a result which we find surprising. As expected, because any redox changes for $Co(CN)_6^{3-}$ are at potentials far removed from those of the other nucleophiles, any intervalence transitions for it are expected to lie at energies higher than those we have been dealing with. A band of high intensity ($\epsilon = 3.0 \times 10^3$ M⁻¹ cm⁻¹) is observed at 380 nm. It is not clear whether this transition involves Os(IV) → Co(III) charge transfer or the reverse. That the former is a possibility is suggested by the observation that Os(IV)–Fe(III) shows absorption, having all the characteristics of that arising from intervalence transfer, at 656 nm, and this can reasonably only be attributed to Os(IV) → Fe(III) charge transfer. If Os(IV) → Co(III) transfer is the origin of the intervalence band observed for Os(IV)–Co(III) and if the Franck–Condon barriers in the two systems are assumed to be the same, E° for the $Co(CN)_6^{3-/4-}$ couple is calculated as −1.0 V. This result, however, cannot be expected to bear any simple relation to experimental measures of E° for this couple. When $Co(CN)_6^{3-}$ is reduced, an antibonding electron is added and the attendant distortions which stabilize the 2+ state are not expected to be simple harmonic.

The appearance of an intervalence band for Os(IV)–Fe(III) at rather low energies suggests that 1e⁻ oxidation of $[Os(en)_2H]^{3+}$ also takes place at rather low potentials. Experiments to find such oxidation at an electrode are vitiated because in the low-potential region $[Os(en)_2H]^{3+}$ is apparently converted to $[Os(en)_2(\eta^2\text{-}H_2)H_2O]^{2+}$.

The interpretation of the absorption in the visible region as arising from Fe(II) → Os(IV) charge transfer provides a ready explanation of the shifts to higher energy observed in acidic and in alkaline solution. As to the former, we ascribe it to protonation of $Fe(CN)_6^{4-}$, which raises the redox potential of the $Fe(CN)_6^{3-/4-}$ couple. The decrease in pK_a from 4.17, when $HFe(CN)_6^{3-}$ is free,[4] to 1.2, when it is ligated to the osmium center, is, qualitatively at least, in harmony with the the inductive effect of the high charge on the cation. If, as we believe, the Os(IV) species has a coordination number of 7, the the moiety $[Os(en)_2(H)Fe(CN)_6]^-$ must be ligated to a water molecule. The change in color from

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[13] Hush, N. S. *Progr. Inorg. Chem.* **1967**, *8*, 357.

[14] Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

blue to rose at high pH then is attributable to the deprotonation of the water molecule. Replacement of H_2O by OH^- decreases the Os(IV)/Os(III) redox potentia and thus is expected to result in a shift of the absorption maximum to higher energy. The value of $pK_a \sim 12$ indicated by our observations is very high for a tripositive cation with the metal center in the oxidation state 4+. The moderation of the inductive effect of the Os(IV) metal center which this indicates is attributable to the presence in the coordination sphere of the very polarizable entity H^- as well as a tetranegative anion.

The observations on the changes in band maxima and the increases in the value of the extinction coefficients brought about by the addition of Cl^- and SO_4^{2-} to Os(IV)–Fe(II) provide strong support for the conclusion[3] that the coordination number of the Os(IV) center is 7. Because the changes are slow, we can conclude that substitution is involved rather than outer sphere association. Replacement of ligated $Fe(CN)_6^{4-}$ would involve loss of the oscillator providing the color. If, however, a water molecule is being replaced, a change in ϵ is not unexpected, and because a substantial increase rather than decrease is observed, the outcome is rather unambiguous on the conclusion we draw, even though we cannot explain why ϵ increases.

The approximate doubling observed when sufficient $Fe(CN)_6^{4-}$ is supplied is even stronger evidence supporting the conclusion regarding the coordination number of the metal.[3] The changes in absorption described as "aging" may well be closely related to the effect observed with $Fe(CN)_6^{4-}$, the difference being that $Fe(CN)_6^{4-}$ already ligated to Os(IV) replaces water on another molecule, leading to the formation of polynuclear species. All the observations we have made, namely the approximate doubling of the extinction coefficient and the kinetic behavior, conform at least qualitatively to this interpretation.

Because some substitution reactions for $[Os(en)_2(H)]^{3+}$ are quite slow, it is not surprising that the immediate products of the $2e^-$ oxidation of **1** by different oxidizing agents species are not always identical. This aspect of the work was touched on only lightly, and will be an important facet of research to be continued on the reaction kinetics. Preliminary studies indicate very large differences in rates of oxidation of $Os^{II}(en)_2(\eta^2\text{-}H_2)L$, depending on the identity of L, and also in the further oxidation of the $[Os(IV)\text{–}H^-]$ species. As to our conclusions thus far on the nature of the product of the oxidation of **1** by O_2, $S_2O_8^{2-}$, and $FeCp_2^+$, it is likely that the last two agents yield the same product, which, in view of the nature of $FeCp_2^+$, we take to be $[Os(en)_2(H)(H_2O)_2]^{3+}$. The absorption characteristics of the product when O_2 is oxidant are noticeably different, and it is possible therefore that at least some of the H_2O_2 generated is ligated to Os(IV).

As far as we know, the polynuclear formation by clustering of $[Os(en)_2H_2]^{2+}$ or $[Os(en)_2H]^{3+}$ around $Fe(CN)_6^{4-}$, in the first case leading to a hexanuclear product and in the second, for which a limit may not have been reached, to a tetranuclear, has not been reported in the literature. Fully substitutionally labile coreagents would lead to intractable solids, and were a fully substitionally inert coreagent used, the reactions would be impractically slow. The two reagents we have used have the advantage that at least one ligand (namely H_2O) is labile, but the other positions resist substitution. Obviously, $[Ru(NH_3)_5H_2O]^{2+}$ also satisfies these requirements, and the subject invites further investigation.

At the present stage of their exploration, the redox characteristics of **1** and related molecules are puzzling. Thus, when **1** is subjected to cyclic voltammetry, the couple $[Os(en)_2(H_2)H_2O]^{3+/2+}$ is registered, at least when the solution is acidic and the sweep rate is high. Reaction with solution reagents, however, shows no hint of the formation of $[Os(en)_2(H_2)H_2O]^{3+}$ as an intermediate but proceeds directly to $[Os(en)_2H]^{3+}$. The latter is apparently reduced to **1** by cyclic voltammetry, when the electrode surface is "suitable". Solution reductants, having more reducing potential than the potential at which **1** is reconstituted at an electrode, fail to act on $[Os(en)_2H]^{3+}$, but Zn/Hg does so readily. It appears that H or H^- carriers ($H^+ + (e^-)$, $H^+ + 2e^-$), as may be available at the surfaces of certain solids, are needed for facile transformation of $[Os(en)_2H]^{3+}$ to **1**. Exploration of this aspect of the work continues.

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