Reaction of $[Os(en)_2O_2]^{2+}$ with Photolyzed $[Mo(CN)_8]^{4-}$ in Water

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Introduction

trans-$[Os(en)_2O_2]^{2+}$ is substitution inert with respect to both the en and oxo ligands[1] and is reluctant to undergo oxidation or reduction reactions with common reagents, i.e., H_2O_2 or Fe(II). However, it readily and reversibly forms addition complex ions with certain metal ions which are π electron donors and potential reducing agents[2]. These composite ions have intense charge-transfer absorption bands in the visible region of the spectrum, which have been attributed to electron mobility through bridging oxo ligands. The X-ray crystal structure of one such complex ion with $[Fe(H_2O)_6]SO_4$ has been reported[3] and was shown to contain a linear Fe−O−Os−O−Fe linkage. It is of theoretical and practical interest to understand the bonding in this type of interaction.

While using $[Mo(CN)_8]^{4-}$ as a crystallizing agent for $[Os(en)_2O_2]^{2+}$, it was noted that a deep blue color slowly developed when solutions were exposed to laboratory light. Since there is evidence[4] that the first photolysis product of $[Mo(CN)_8]^{4-}$ is $[Mo(CN)_7OH_2]^{3-}$ it seemed likely that some sort of Mo−O−Os−O entity, similar in bonding to that found with Fe(II), was responsible for the enhanced color. This Note describes experiments used to evaluate the nature of this interaction

An equally important aspect of this investigation has to do with the identification of the primary photolysis product of $[Mo(CN)_8]^{4-}$ using lower energy photons. A variety of products have been suggested[5] and some isolated but the understanding is limited. Using $[Os(en)_2O_2]^{+2}$ to capture the primary photoproduct and prevent further reactions would establish its composition and suggest its structure.

Experimental Section

Materials. *trans*-$[Os(en)_2O_2]Cl_2$ was prepared by the method of Malin and Taube.[6] It was recrystallized at timely intervals as pale yellow crystals from acidic water solution. It darkened over a period of months due to the formation of OsO_2. $K_4Mo(CN)_8{\cdot}2H_2O$ was prepared as previously described[7] and analyzed spectrophotometrically ($\epsilon = 170$ at 386 mμ). It was stable in the solid state. Tetraphenylarsonium chloride ($Q_4AsCl{\cdot}2H_2O$) was crystallized once from water−methanol mixtures. Preparation of the photoaddition complex was accomplished by photolyzing a cold 10^{-4} M aqueous HCl solution containing $Mo(CN)_8^{-4}$ and Q_4AsCl in the approximate concentration region of 0.01 and 0.025 M, respectively. In the absence of light, no precipitation occurred under these conditions. A variety of light sources were used, but bright sunlight was of satisfactory energy and intensity. Upon irradiation the solution turns red due presumably to the formation[8] of $[Mo(CN)_7(OH_2)]^{3-}$. Addition of a saturated solution of *trans*-$[Os(en)_2O_2]Cl_2$ produced an immediate blue solution, which quickly crystallized thin blue platelets of the product. They were collected on a filter, washed with a small amount of cold solution of 1% Q_4AsCl, and dried in a vacuum. In this state the product is suitable for analysis. The yield varied but reached about 95% when the light intensity was high, the acidity 10^{-4}−10^{-3} M, the solution temperature low, and washing kept to a minimum.

Single crystals for X-ray analysis were very difficult to obtain. The only method found, however, produced large crystals, only a few of which were single and showed sharp diffraction out to high 2θ angles. The solid salt was dissolved in a very small amount of 95% ethanol, filtered, and allowed to slowly evaporate in a refrigerator held at about 5 °C. A small amount of water increased the solubility and was necessary for the formation of single crystals. Flat transparent plates were formed which easily lost solvent on exposure to the atmosphere. The single crystals were quickly moved into a heavy mineral oil, mounted on a glass fiber attached to a goniometer head, and cooled to −100° in a nitrogen stream. The crystals were anisotropic in polarized light and highly phototropic. When viewed perpendicular to the major face they appeared a pale tan color. In all other directions they were black unless very, very thin when they were dark blue. It is very likely that two related complexes are formed in this photolysis: the 2-Mo/1-Os described in this paper and a second complex of similar color having 1-Mo/1-Os. The latter has not been isolated and probably is thermodynamically unstable with respect to the former, as has been shown in the Fe^{2+}−$[Os(en)_2O_2]^{2+}$ reaction[2].

Physical Measurements. The UV−vis absorption measurements were recorded on a Perkin-Elmer Coleman 575 spectrophotometer using water-jacketed, temperature controlled quartz cells. The NMR spectra were taken on a GE Nicolet 300 MHz spectrometer using CD_3CN as the solvent and internal standard. The quantum yield was measured using a filtered light source of wavelength 420 mμ and a half bandwidth of 60 mμ. A Kettering YSI radiometer was employed to determine the fraction of light absorbed, and the Fe(III)−oxalate reaction was used as the standard. In most other studies photolysis involved repeated flashes, in a constant geometry, of a photoflash filtered with an IR removing $CuSO_4$ solution. Magnetic measurements were made on a Johnson Matthey magnetic susceptibility apparatus, Wayne PA 19087, at room temperature utilizing about 80 mg solid samples with water and $NiCl_2$ solution as standards.

The mass spectra were obtained on a Finnigan TSQ-7000 spectrometer by the flash-ionization method with methanol solutions. IR spectra were recorded using KBr plates in a Nicolet 500 FT-IR spectrometer.

Analysis for C, H, and N was carried out using commercial methods, Os by neutron activation, Mo by atomic absorption and neutron activation, Q_4As^+ gravimetrically as the ReO_4^- salt, and water by the Carl Fisher method.

Crystallography. The single-crystal X-ray studies utilized a SMART CCD[9] diffractometer with $\lambda = 0.71073$ Å (Mo Kα radiation). The data

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Table 1. Crystallographic Data and Refinement

$[Q_4As^+]_4\ [(CN)_7Mo{-}O{-}Os(en)_2{-}O{-}Mo(CN)_7{}^{-4}]{\cdot}7H_2O{\cdot}2(EtOH)$	
empirical formula	C118 H122 As4 Mo2 N18 O11 Os1
fw	2650.10
temp	173(2) K
wavelength	0.71073 Å
cryst syst, space group	$P-1$
unit cell dimensions	
a	10.978(5) Å
b	13.170(5) Å
c	40.322(17) Å
α	93.501(7)°
β	95.994(7)°
γ	95.638(8)°
volume	5755(4) $Å^3$
Z, calcd density	2, 1.529 mg/m^3
absorption coeff	2.524 mm^{-1}
$F(000)$	2672
cryst size	0.40 × 0.15 × 0.03 mm
θ range for data collection	1.15−27.0, used 1.15−23.26°
limiting indices	$-12 \leq h \leq 11$, $-14 \leq k \leq 14$, $-44 \leq l \leq 44$
refl. collected/unique	26016/14226 [R(int) = 0.0322]
completeness to $\theta = 27.10$	99.0%
max and min transmission	0.934 and 0.432
refinement method	Full-matrix LS on F^2
data/restraints/parameters	16365/0/1374
GOF on F^2	1.262
final R indices [$I > 2\sigma(I)$]	R1 = 0.0639 wR = 0.1265
R indices (all data)	R1 = 0.0759 wR = 0.1214
largest diff peak and hole	1.282 − 1.924 e/A^{-3}

collection nominally covered over a hemisphere of reciprocal space by a combination of three sets of exposures at different ω values, and each exposure covered 0.3° in ω. Coverage of the unique set was over 97% complete to $2\theta = 54°$. Corrections were made for absorption and decay using SADABS,[10] the latter by repeating the initial intensity frames at the end of data collection and analyzing the duplicate reflection intensities. The crystallographic data and refinement of the Q_4As^+ salt of the complex as the heptahydrate containing two ethyl alcohol molecules are described in Table 1. All heavy atoms were refined anisotropically (SHELXL),[11] and all hydrogens, except for those on the water oxygens, were easily located in difference maps. The hydroxyl hydrogens in the alcohol were refined isotropically. In the final LS calculations, the hydrogen atom positions in the ions were calculated and given values of $\beta = 1.3 \times \beta$(heavy atom to which attached). Water hydrogens were not included in the LS calculation. Graphics utilized XSEED[12] and ORTEP3.[13]

Results and Discussion

Reaction of $[Mo(CN)_8]^{4-}$ + Light with $[Os(en)_2O_2]^{2+}$. Photolysis of yellow $[Mo(CN)_8]^{4-}$ solutions with light of wavelength 4800−4000 Å leads to an orange−red species, ϵ_{max} at 4100 Å, thought to be $[Mo(CN)_7(OH_2)]^{3-}$. This reacts rapidly with aqueous $[Os(en)_2O_2]^{2+}$, producing a blue ion, *bis*-(heptacyanomolybedenum(IV) μ,μ-*trans*-dioxo-*bis*-ethylenediamineosmate(VI), (Mo−O−Os−O−Mo), with an intense visible absorption, ϵ_{max} at 6950 Å (water), 7000 Å (MeOH). At the radiation wavelength, concentration and path length used only a small fraction of the incoming beam of light, and about 95% of it was absorbed by $[Mo(CN)_8]$.$^{4-}$ The product ion, while strongly absorbing light, was at least 5 times more stable than $[Mo(CN)_8]^{4-}$. However, photons of higher energy are quite effective in causing further reaction. Photolyzed $[W(CN)_8]^{4-}$ behaves in an analogous fashion, with ϵ_{max} at 5550 Å, while $[Re(CN)_8]^{3-}$ (? see later) forms an adduct with $[Os(en)_2O_2]^{2+}$, with ϵ_{max} at 4500 Å.

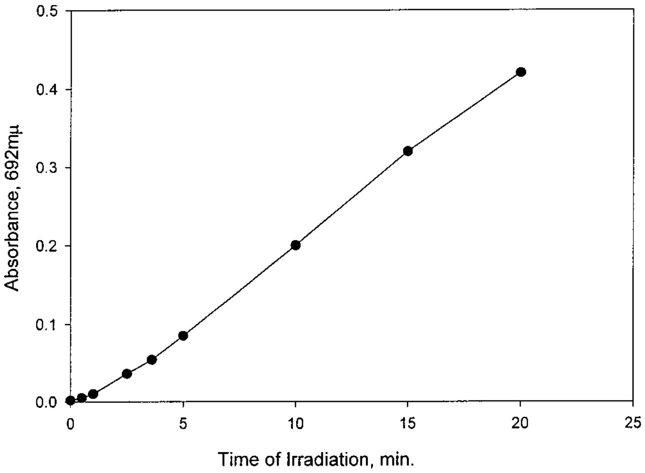

Figure 1. Absorbance Changes as a function of amount of light. Irradiation of $[Mo(CN)_8]^{4-}$ + $[Os(en)_2O_2]^{2+}$, 10^{-4} M H^+.

Both the ^1H and ^{13}C NMR gave sharp peaks for Mo−O−Os−O−Mo, confirming the diamagnetism of both metal ions and thus their oxidation state. ^1H: CH_2(2) 3.28, NH_2 (2) 5.64, Q (22) 7.67−7.90, (assignment, intensity, ppmd). ^{13}C: CN 1 122.45, CH_2 (1) 50.93, Q (4) 130.5−135.8 (assignment, number, ppmd). No other resonances, except those due to the solvent, were detected. The bulk magnetic susceptibility showed it to be diamagnetic, $X_g = -2.8 \times 10^{-6}$ cgs.

All of the analyses were on samples dried at 21° under vacuum. They were consistent with the trimetallic complex containing four Q_4As^+ and three waters of hydration. Note that the X-ray structure unit cell of the crystals obtained contained 7 H_2O's and 2 ethanols and easily lost solvent on standing. Calculated for: $(Q_4As)_4[Mo(CN)_7{-}O{-}Os(en)_2{-}O{-}Mo(CN)_7]{\cdot}3H_2O$, 2485.95: C, 55.07; H, 4.14; N, 10.14; Os, 7.65; Mo, 7.72; Q_4As^+, 61.68; H_2O, 2.17%. Found: C, 56.06; H, 4.21; N, 9.52; Os, 7.16; Mo, 7.45 (na), 7.50 (aa); Q_4As^+, 61.40; H_2O, 2.35%.

Since Mo−O−Os−O−Mo is very insoluble in water in the presence of excess Q_4As^+, it was possible to estimate the "ideal percent yield" in the formation reaction. A solution, (pH = 4) containing an excess of $[Mo(CN)_8]^{4-}$, Q_4AsCl, and a known weight of $[Os(en)_2O_2]^{2+}$ was cooled to 10° and continuously flushed with nitrogen gas to remove HCN formed. Then it was irradiated with a series of filtered photoflashes until no further blue color developed. After an hour at 5°, the blue precipitate was collected on a sintered glass filter, dried, and weighed. Two trials gave a yield of 95.3(8)%.

The intensity of absorption at 6920 Å due to the formation of Mo−O−Os−O−Mo was proportional to the number of photons absorbed by $[Mo(CN_8\ ]^{4-}$ (time of irradiation of a standard source of light or the number of flashes of a filtered photoflash under constant geometry). An example is given in Figure 1. Less than 10% of the $[Mo(CN)_8]^{4-}$ or $[Os(en)_2O_2]^{2+}$ was consumed. The linear nature of the absorbance/flash and the near zero intercept at time zero strongly suggests that the mono- complex is not formed in significant amounts even when $[Os(en)_2O_2]^{2+}$ is in large excess.

The quantum yield of Mo−O−Os−O−Mo using 4200 Å light based on two $Mo(CN)_7$ entities per molecule and a

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molecular absorbance of 1.85(10) × 10^5 was 0.95(4). The measurements were carried out in 10^{-4} M H^+ to prevent recombination, and the computation utilized a correction for the dissociation of Mo−O−Os−O−Mo.

Mo−O−Os−O−Mo partially reversibly dissociates into $[Mo(CN)_7OH_2]^{3-}$ and $[Os(en)_2O_2]^{2+}$ in water solution. The dissociation constant was evaluated by measuring absorbance changes at 6920 Å which occurred upon photogenerating known amounts of $[Mo(CN)_7OH_2]^{3-}$ in equilibrated solutions of Mo−O−Os−O−Mo. The values of K_f = [Mo−O−Os−O−Mo]/ $([Mo(CN)_7OH_2]^{3-})^2$ $([Os(en)_2O_2]^{2+})$ were reasonably constant and had a value of 4.5(3) × 10^9 at 10°. This constant does not take into account the mono- complex that probably exists to some limited extent. However the data did not suggest that this was of high significance.

The primary photoreaction $[Mo(CN)_8]^{4-} \rightarrow [Mo(CN)_7OH_2]^{3-} + CN^-$ followed by $CN^- + H_2O \rightarrow HCN + OH^-$ takes place rapidly. Attempts to follow this rate by pH measurement showed all pH electrodes to be much to slow responding compared to the reaction rate. Using faster conductivity measurement, the rate of this reaction was shown to give a $t_{1/2}$ less than 0.15 s at 25°. The assumption that $[Mo(CN)_7OH_2]^{3-}$ is the sole photoproduct is justified by the quantum yield and composition of Mo−O−Os−O−Mo.

The reaction $2[Mo(CN)_7OH_2]^{3-} + [Os(en)_2O_2]^{2+} \Leftrightarrow$ Mo−O−Os−O−Mo is reversible and somewhat slower. The approach to equilibrium, followed spectrophotometrically at 6920 Å, shows first-order behavior with a half-life of ∼20 s at 10° and concentrations of approximately 5 and 2 × 10^{-5}M, respectively. This value is not of mechanistic use and only indicates the qualitative reaction velocity. The reacting species of Mo is probably $[Mo(CN)_7OH_2]^{3-}$ since no significant change in the rate of formation or the extent of reaction occurs if $[Os(en)_2O_2]^{2+}$ is present when the light flash occurs or if its addition is delayed by a minute. A delay of 10−15 min, however, diminishes the amount of trimer formed due to either further reaction or recombination. The formation reaction route is most likely the stepwise reaction of $[Os(en)_2O_2]^{2+}$ with $[Mo(CN)_7OH_2]^{3-}$ in two steps facilitated by the very large second formation constant. Reaction of $[Mo(CN)_7O{-}Os(en)_2{-}O]^{1-}$ with $[Mo(CN)_8]^{4-}$ by cyanide ion replacement is ruled out by the observed quantum yield of nearly unity per Mo complex used.

Mass spectral measurements were not useful. Even with mild spray ionization, only the M/e peaks of the Q_4As^+ were observed. This is not unusual for a highly charged multimetal complex ion.

Infrared absorption spectra have a single CN stretch at 2115 cm^{-1} compared to those of $[Mo(CN)_8]^{4-}$ at 2100, 2124 cm^{-1}. Intense bands at 1605, 1075, 740, and 630 cm^{-1} serve as identification of the Q_4As^+ salt of Mo−O−Os−O−Mo. The 1075 cm^{-1} band can probably be identified with the Os═O bond and is at lower energy than in the parent or its Fe(II) complex.[2]

Structure of $(Q_4As)_4[Mo(CN)_7{-}O{-}Os(en)_2{-}O{-}Mo(CN)_7]\cdot 7H_2O\cdot 2C_2H_5OH$. The unit cell contains four independent tetrahedral Q_4As^+ ions containing nearly ideal bond distances, angles, and planar rings. Even the ethyl alcohols are well defined. The water oxygens have good temperature factors but, as usual, their hydrogen atoms could not be located. The final agreement factor of 6.4% is appropriate for a structure containing 154 heavy atoms. Most of the residual electron density resides near the heavy metals.

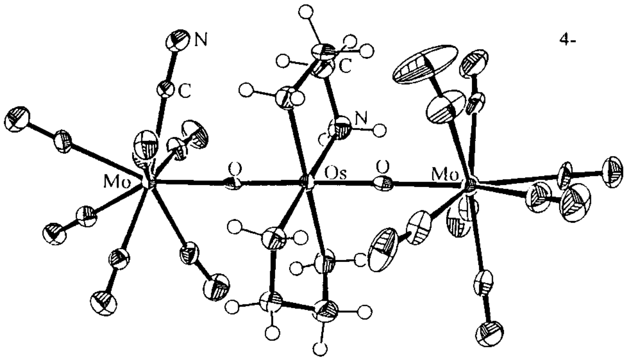

Figure 2. Ortep drawing, 50% ellipsoids, of $[(CN)_7Mo{-}Os(en)_2OMo(CN)_7]^{4-}$ as the Q_4As^+ salt.

Table 2. Average[a] Bond Distances (Å) and Angles (deg)[b]

bond(s)	Mo−Os−Mo	$[Mo(CN)_8]^{4-}$	$[Os(en)_2O_2]Cl_2$[b]
$C{-}N_{ave.}$	1.145(7)	1.151(12)	
Mo−C−N	174.2(20)	177.4(4)	
Os−N	2.083(11)		2.11(1)
O−Os−O	177.6(3)		180.0(0)
Mo−C	2.170(11)	2.159(11)	
Os−O	1.829(3)		1.74(1)
Mo−O	1.961(4)		
Mo−Os−Mo	175.8(6)		
Os−O−Mo	172.9(30)		
Mo−Os	3.78(3)		

[a] From a recent (R.K.M., unpublished) X-ray determination of $[Pt(en)_2]_2[Mo(CN)_8]\cdot 7H_2O$, which is more accurate than earlier data. [b] Reference 1.

The anion, shown in Figure 2, is a discrete linear arrangement of Mo−O−Os−O−Mo complex ions bonded through the *trans*-osmyl oxygens. There are two $Mo(CN)_7$ entities per $[Os(en)_2O_2]^{+2}$. The bond angle, Mo−O−Os−O−Mo, is 175.8(6)°, essentially linear. The osmium(VI) complex is nearly identical to that in $[Os(en)_2O_2]Cl_2$[1] except for elongated metal−oxygen bonds. A comparison is given in Table 2 , where it is seen that Os═O expands from 1.74(1) to 1.829(3) Å, a rather remarkable change. The ethylenediamine ligands are in the gauche configuration. The Os−N bond distances are essentially unchanged from the parent ion. The molybdenum complex is eight coordinate with seven carbon bonded cyanide ions and the oxygen of the osmium complex. Coordination around the Mo is only slightly distorted from the dodecahedral (D_{2d}) found[14] in the octacyano complex ion. The Mo−O bond distance is 1.961(4) Å, a rather short bond considering the bond to CN^- is 2.170(11) Å. No change in the Mo−C distance averages is noted in the two structures compared in Table 2. The $Mo{-}C{-}N_{ave}$ angles decrease about 3° in Mo−O−Os−O−Mo compared to $Mo(CN)_8^{4-}$, as the CN nitrogen bends toward the en ligand. Thus, there is a strong reversible association between $[Mo(CN)_7]^{3-}$ and *trans*-$[Os(en)_2O_2]^{2+}$ through the yl oxygens, which results in a major change in their bond lengths. One may consider the linear array to approach Mo═O═Os═O═Mo. There are no significant hydrogen bonds between amine hydrogen atoms and cyanide N. In Fe(II)−O−Os(en)₂−O−Fe(II),[3] a similar linear arrangement exists accompanied by the intense light absorption in the 6000 Å region of the spectrum. The Os−O distance is also elongated to 1.845(7) from 1.734(7) Å (in the same crystal structure), and the Fe−O−Os angle is 174.4(30)°. The Fe−O distance is shorter than expected, 1.800(6) compared to 2.05 Å in other single bonded structures.

The structure of Mo−O−Os−O−Mo strongly suggests that the primary aqueous photolytic product of $[Mo(CN)_8]^{4-}$, using

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(14) Hoard, J. L.; Nordsuck, H. H. *J. Am. Chem. Soc.* **1939**, *61*, 2853.

light in the visible region of the spectrum, is $[Mo(CN)_7OH_2]^{3-}$. It has considerable stability and changes only slightly over a period of at least 10 min and probably much longer. In the presence of $[Os(en)_2O_2]^{2+}$, it is rapidly captured and converted to the stable Mo−O−Os−O−Mo complex ion. At equilibrium, little of the 1/1 complex is found because it is thermodynamically much less stable than the 2/1 ion. Tungsten in $[W(CN)_8]^{4-}$ behaves in an identical fashion, and the Fe(II)-$[Os(en)_2O_2]^{2+}$ system is very similar. As stated earlier, similar behavior is observed on irradiation of preparations of $[Re(CN)_8]^{3-}$ in the presence of $[Os(en)_2O_2]^{2+}$, but it is not clear that an analogous product is formed. However, the evidence for $Re(CN)_8{}^{3-}$ itself is weak,[15] and our attempts at establishing its existence in preparations using literature methods have so far been unsuccessful.

Support for $[Mo(CN)_7OH_2]^{3-}$ being the primary photolysis product is the isolation of $[W(CN)_7O{-}O]^{3-}$ and the Mo analogue as the Co(III)−sepulcherate salts, Figure 3. $[W(CN)_7OH_2]^{3-}$, prepared by the photolysis of $[W(CN)_8]^{4-}$, is air sensitive, slowly forming the $(CN)_7W(VI)$−peroxide complex ion, which crystallizes in the presence of the complimentary charged $[Co(sepulcherate)]^{3+}$. The oxygens are side bonded to a single coordination position of the metal. All seven CN^-'s are retained in this oxidation−reduction. Thus, future photolytic reactions on these octacyano complexes should be conducted in the absence of O_2. The yl oxygens of $[Os(en)_2O_2]^{2+}$ are very weak σ donors,[1] as evidenced by their lack of interaction with H^+. However, they are strong π acceptors from some metal ions in lower oxidation states. What is especially surprising is that complexing of one oxygen enhances the coordinating ability of the oxygen trans to it.

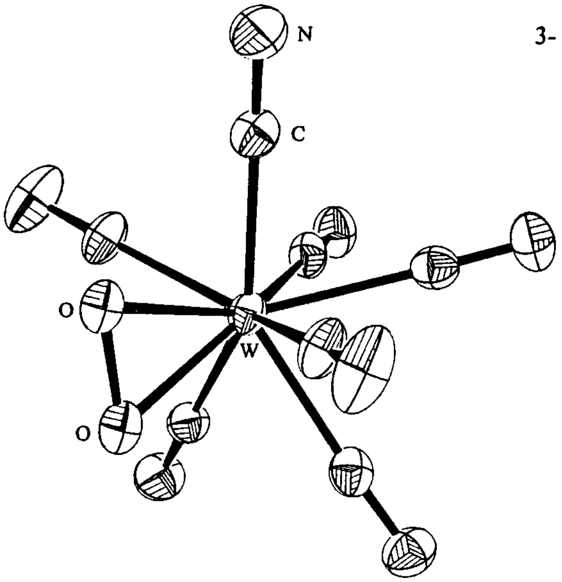

Figure 3. Crystal structure of $[Co(sepulcherate)][W(CN)_7O_2]\cdot 4H_2O$. Anion only.

Summary

The primary photolytic product of the irradiation of aqueous $[Mo(CN)_8]^{4-}$ with 4000−4800 Å light is $[Mo(CN)_7OH_2]^{3-}$. It reacts rapidly with *trans*-$[Os(en)_2O_2]^{2+}$ to form linear $[(CN)_7Mo{-}O{-}Os(en)_2{-}O{-}Mo(CN)_7]^{4-}$, a highly colored ion which can be crystallized as the Q_4As^+ salt. It has an extremely intense charge-transfer light absorption band centered at 6950 Å and a Mo−O−Os−O−Mo angle of 175.8(6)°. The Os−O bond length is elongated 1.74(1) → 1.829(3) Å, showing a strong interaction. Evidence for the 1/1 complex was not found, suggesting instability compared to the 2/1 ion.

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Supporting Information Available: Crystallographic data for the structures (2) reported in this paper in CIF format; these have also been deposited with the Cambridge Crystallographic Data Center as supplementary publication No.162771 $(Q_4As)_4[Mo(CN)_7{-}O{-}Os(en)_2{-}O{-}Mo(CN)_7]\cdot 7H_2O\cdot 2EtOH$, and No. 162772 $[Co(sepulcherate)][W(CN)_7O{-}O]\cdot 4H_2O$ (copies can be obtained on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax, (0)-1223−336033; e-mail, deposit@ccdc.cam.ac.uk)). This material is available free of charge via the Internet at http://pubs.acs.org.

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