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Photoinduced multielectron charge transfer in the polymetallic intervalent complex $[(NC)_5Fe\text{-}CN\text{-}Pt(NH_3)_4\text{-}NC\text{-}Fe(CN)_5]^{4-}$ and related species

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Abstract

The complex anion, $[(NC)_5Fe^{II}\text{-}CN\text{-}Pt^{IV}(NH_3)_4\text{-}NC\text{-}Fe^{II}(CN)_5]^{4-}$, is synthesized from the redox reaction of $K_3Fe(CN)_6$ and $Pt(NH_3)_4(NO_3)_2$ in aqueous solution. Irradiation of the intervalent (IT) absorption band of the complex effects a net two electron transfer, regenerating the molecules from which it was formed. The IT band energy can be modulated by changing the cyanometalate species employed or through the use of a noncoordinating solvent such as DMSO. The photochemistry of the polymeric "$(\text{-}Fe\text{-}Pt\text{-})_n$" cyanide-bridged complex is also discussed.

1. INTRODUCTION

Mixed valence (MV) compounds, i.e. complexes which contain both a donor and an acceptor moiety, are important to a number of fields of chemistry, including electron transfer, artificial photosynthesis, supramolecular photochemistry, and molecular electronics [1]. These species are of inherent interest because they possess intervalent (IT) or metal-to-metal (MMCT) charge transfer absorption bands in the low energy (visible or near-IR) regions of their spectra. Irradiation of these bands formally corresponds to a photoinduced electron transfer which is directed in space along the axis connecting the interacting metal centers. In the past forty years, hundreds of binuclear MV complexes have been synthesized, beginning with the synthesis of the Creutz-Taube ion, $[(NH_3)_5Ru^{II}\text{-}pyz\text{-}Ru^{III}(NH_3)_5]^{5+}$, in 1969 (pyz=pyrazine) [2]. Homobinuclear MV transition-metal complexes generally absorb in the near-IR region of the spectrum due to the redox symmetry of their metal centers. This fact is an experimental manifestation of the Hush equations [3] developed in the 1960's, namely that the optical IT energy (E_{op}) is equal to the sum of the reorganization energy (λ) associated with transferring the electron between the metal centers and the free energy difference (ΔE_0) between their ground state potential wells. Heterobinuclear complexes, on the other hand, often occur in the visible portion of the spectrum, and are therefore more accessible to conventional sources of photochemical irradiation. Despite the relatively large number of binuclear complexes examined, relatively few trinuclear MV species have been synthesized [4]; and none of these have exhibited photochemistry involving all three metal centers, as observed for the complex of interest.

2. RESULTS AND DISCUSSION

2.1 $\{[Pt(NH_3)_4]_2^{4+}\}\{[(NC)_5M^{II}\text{-}CN\text{-}Pt^{IV}(NH_3)_4\text{-}NC\text{-}M^{II}(CN)_5]^{4-}\}$:

The complexes $\{[Pt(NH_3)_4]_2^{4+}\}\{[(NC)_5M^{II}\text{-}CN\text{-}Pt^{IV}(NH_3)_4\text{-}NC\text{-}M^{II}(CN)_5]^{4-}\}$ (M=Fe, Ru, or Os) were synthesized by the redox reaction of the oxidized cyanometalate with tetraammineplatinum (II) [5]. The oxidation states of these species as M(II)/Pt(IV)/M(II) were confirmed by the presence of bridging and nonbridging M(II) cyanide stretches and both Pt(II) and Pt(IV) ν(NH) stretches in the IR, as well as by cyclic voltammetry. The electronic spectrum of each of these complexes contains a new, broad absorption band in the UV or visible portion of the spectrum which is accordingly assigned as intervalent (IT) charge transfer from M(II)→ Pt(IV). The energies of the IT bands for both this series of compounds and the series described in the following section are summarized in Table 1 below. The ground state redox potentials of the cyanometalates are also listed (the redox potential of M within the complexes is shifted positive by about 360 mV) [6]. It can be seen from the data in Table 1 that the Hush equations are satisfied; that is, as the redox potential of the cyanometalates shifts more positive, the IT absorption maximum shifts to higher energies. Figure 1 depicts the electronic absorption spectra of this series of compounds.

Table 1
Redox potentials (cyanometalates only) and IT absorption energies of $[(NC)_4LM\text{-}CN\text{-}Pt(NH_3)_4\text{-}NC\text{-}M(CN)_4L]^{n-}$ mixed valence complexes

M	L	IT band (nm)	E_R (V vs SCE)
Fe	CN	424	0.19
Ru	CN	354	0.73
Os	CN	380	0.45
Fe	4,4'-bipyridine	424	0.26
Fe	pyrazine	418	0.31
Fe	4-cyanopyridine	416	0.32
Fe	2-pyrazinecarboxylic acid	410	0.38
Fe	2-fluoropyridine	399	0.48
Fe	N-methylpyrazinium	393	0.54

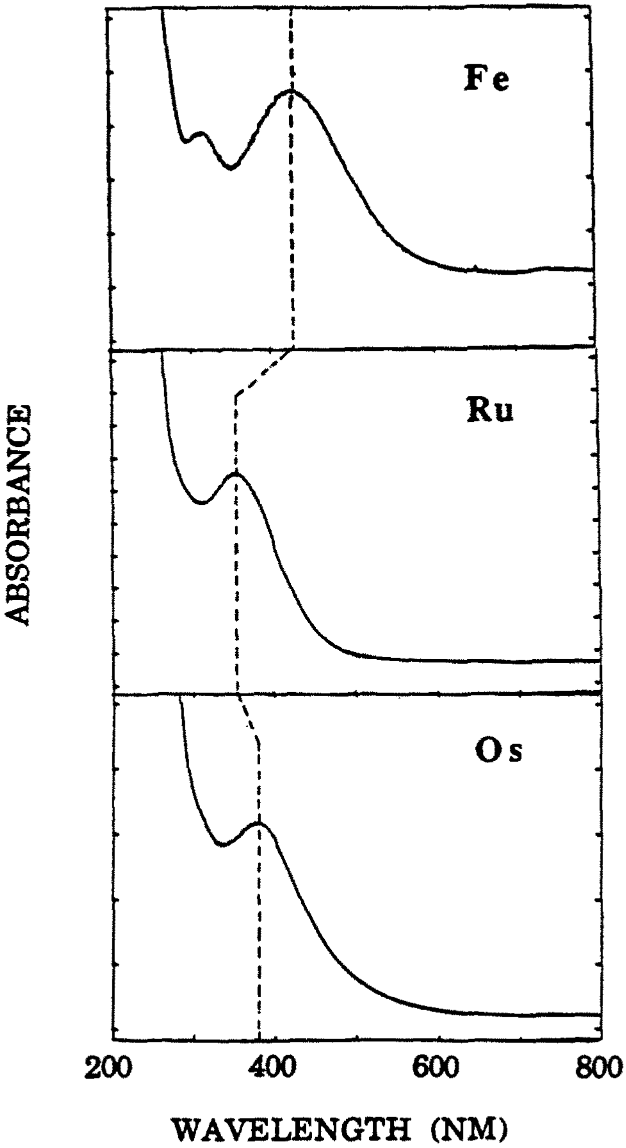

Figure 1. UV-vis absorption spectra for $\{[Pt(NH_3)_4]_2^{4+}\}\{[(NC)_5M^{II}\text{-}CN\text{-}Pt^{IV}(NH_3)_4\text{-}NC\text{-}M^{II}(CN)_5]^{4-}\}$, where M=Fe (top), Ru (middle), and Os (bottom).

The species $\{[Pt(NH_3)_4]_2{}^{4+}\}\{[(NC)_5Fe^{II}\text{-}CN\text{-}Pt^{IV}(NH_3)_4\text{-}NC\text{-}Fe^{II}(CN)_5]^{4-}\}$ photochemically undergoes a net two electron transfer process when irradiated at 488 nm (on the red side of its IT absorption band) in aqueous solution. The photoproducts have been determined spectroscopically as ferricyanide and tetraammineplatinum (II) [5]; that is, the species from which the complex was formed initially by a thermal electron transfer. The equivalent one electron charge transfer reaction has been reported for Co(III)-M(II) cyanide-bridged complexes [7]. The quantum yield for the photoprocess of interest, as based on the moles of ferricyanide produced, is 0.02. This value is relatively wavelength independent over the range of 460–560 nm. This transformation can be monitored using UV-vis spectroscopy as illustrated in Figure 2. Since the products of this reaction back react to form the trinuclear species, a photostationary state can be established for this system by adjusting the initial concentrations of $Fe(CN)_6{}^{3-}$ and $Pt(NH_3)_4{}^{2+}$ employed.

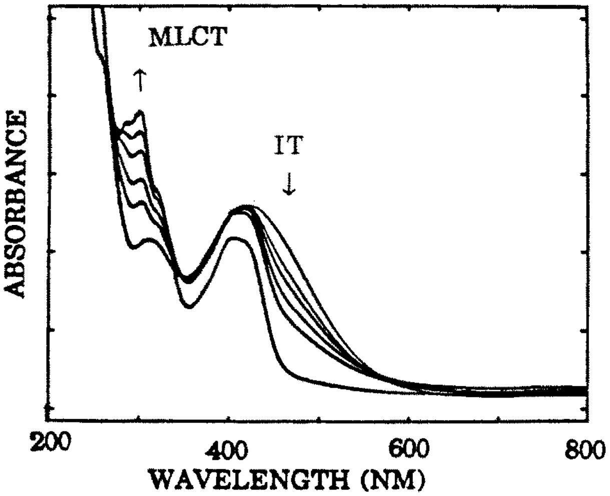

Figure 2. Electronic absorption spectra of $\{[Pt(NH_3)_4]_2{}^{4+}\}\{[(NC)_5Fe\text{-}CN\text{-}Pt(NH_3)_4\text{-}NC\text{-}Fe(CN)_5]^{4-}\}$ in aqueous solution as a function of photolysis (488 nm) time. The arrows indicate the growth and decline of peaks with time.

The charge transfer photochemistry of species I is not limited to aqueous solution. The anionic complex can be electrochemically derivatized onto a nickel electrode surface to form a chemically modified electrode [8]. Diffuse reflectance infrared spectroscopy of the surface confined species indicates that its structure is unchanged except for the fact that it forms coordinative covalent (dative) bonds with the electrogenerated Ni^{2+} ions through the lone pairs on the terminal cyanide nitrogen atoms. The resulting surface is amorphous as determined by Xray diffraction and exhibits a single redox wave associated with the ferrous units of the complex which is insensitive to the intercalated cation required for electroneutrality. Irradiation of the orange surface at 488 nm effects a photoinduced electron transfer process similar to that of the complex in solution. The resulting yellow surface is crystalline as determined by Xray diffraction and is electrochemically sensitive to the intercalated alkali cation. Infrared spectroscopy, along with the Xray and electrochemical data, show that the new surface is identical to the chemically modified nickel ferricyanide electrode. The Pt(II) tetraammine generated by the photoprocess remains trapped in the crystalline lattice if the photoreaction is done in air; however, it dissolves out of the surface lattice if the process is performed in solution. The photochemical transformation of the amorphous lattice into a microcrystalline one which is electrochemically cation sensitive offers one unique control of the charge transfer free energies of the surface species [8].

In the cases where M=Ru or Os, the trinuclear anions are photochemically inert. An analysis of the thermal and activation barriers within these complexes on the basis of Hush theory has recently been reported [6]. It can be shown, on the basis of these data, that once the photoexcited "M(III)-Pt(III)-M(II)" is accessed, the rate constant for the formation of products is three orders of magnitude smaller for Os than for Fe. At the same time, the thermal reaction to regenerate the trinuclear complex is also favored in the Os case by a lower activation barrier. In the case of Ru, the tendency toward reforming the trinuclear complex is even more pronounced. Therefore, the observed lack of photochemistry for these two complexes can be explained in terms of the competing activation barriers once the photochemical intermediate has been formed.

However, it has also been shown that the relative free energies of the trinuclear species and their mononuclear redox isomers can be modulated by employing a noncoordinating solvent such as DMSO [6]. It has long been known that the redox potential of ferri/ferrocyanide varies significantly depending on the electrochemical solvent employed [9]. Solvents such as water which can interact with the lone pairs on the cyanide nitrogen atoms shift the redox potential of the iron complex more positive than in aprotic solvents such as DMSO. Since the redox potential of tetraammineplatinum (II) is expected to be relatively unchanged by the solvent sphere, it was speculated that the redox potentials of the Fe and Pt moieties within the trinuclear complexes could be modulated by employing different DMSO/water mixtures. This was indeed found to be the case; in fact, in increasing mole fractions of DMSO/water, the redox potentials of the Fe and Pt units within the complex actually "crossed over" so that the Pt(IV) moiety oxidized the two ferrous units, forming two moles of ferricyanide and one mole of tetraammineplatinum (II). By adjusting the ratios of DMSO/water mixtures for the Os and Ru trinuclear complexes, one can modulate the relative activation barrier heights for the photochemical and thermal electron transfer processes such that the photochemical reactivity of these species is now possible.

The polymeric "$(\text{-Fe}^{II}\text{-Pt}^{IV}\text{-})_n$" species is synthesized by the oxidation of complex **I** at a potential of 1.4 V vs SCE in an excess of Pt(II). The IT absorption band of the soluble portion (probably low molecular weight oligomers) of the polymer is blue-shifted from that of the trinuclear complex. Irradiation of this species does not lead to productive photochemistry. This may be a combination of the increased activation barrier of the photochemically forward electron transfer process and the probable rigidity of the bridged lattice.

2.2 $Na_2[(NC)_4LFe^{II}\text{-}CN\text{-}Pt^{IV}(NH_3)_4\text{-}NC\text{-}Fe^{II}L(CN)_4]$:

The species $Na_2[(NC)_4LFe^{II}\text{-}CN\text{-}Pt^{IV}(NH_3)_4\text{-}NC\text{-}Fe^{II}L(CN)_4]$, where L=substituted pyridine or pyrazine, were synthesized and characterized along similar lines to the compounds discussed in the preceding section. The energies of the IT absorption bands of these complexes were also found to vary linearly with the change in free energy of their ground state potential surfaces. This result is in agreement with Hush theory for MV complexes, assuming identical reorganization energies. The redox potentials of the cyanometalate species and the IT absorption energies of their trinuclear counterparts are listed in Table 1. In addition to the IT bands of these species, the appearance of MLCT [Fe(II)→L] absorption bands also occur in the visible portion of their electronic spectra, often overlapping the IT bands (although several are completely distinguishable).

Irradiation of the IT bands of the species where L=4-cyanopyridine leads to the formation of the oxidized ferric complex and tetraammineplatinum (II) as observed in the preceding section for the iron species. The photochemistry of the remaining complexes was not investigated; however, the identical nature of the photoprocess of this complex with that observed in the above section indicates that all of the compounds under investigation probably undergo similar photoinduced electron transfer processes.

3. ACKNOWLEDGEMENTS

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