Optical Outer-sphere Metal to Metal Charge Transfer in the Ion Pairs $[Pt(NH_3)_5Cl]^{3+}[M(CN)_6]^{4-}$ with M = Fe, Ru and Os

ARND VOGLER* and HORST KUNKELY

Institut für Anorganische Chemie, Universität Regensburg, Universitätsstrasse 31, D-8400 Regensburg, F.R.G.

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Ion pairs of transition metal complexes which contain a reducing and an oxidizing metal center are frequently characterized by metal to metal charge transfer (MMCT) bands in their absorption spectra [1–4]. These spectroscopic properties are of particular interest with regard to intermolecular photoredox processes [1–4]. Ion pairs with Pt(IV) as the oxidizing component have not yet been observed to display MMCT bands. For example, the salt $[Pt(NH_3)_4]^{2+}[PtCl_6]^{2-}$ was reported to show no evidence for mixed-valence interaction [5]. This is quite surprising since the intense color of some solid Pt(II)/(IV) mixed-valence materials such as Wolffram's red and related compounds is caused by low-energy MMCT transitions from Pt(II) to Pt(IV) [6]. In the present communication we describe the occurrence of MMCT bands in the electronic spectra of ion pairs which contain $[Pt(NH_3)_5Cl]^{3+}$ as oxidizing complex.

When the colorless aqueous solutions of $[Pt(NH_3)_5Cl](ClO_4)_3$ [7] and $K_4[M(CN)_6]$ [8] with M = Fe, Ru and Os were mixed a yellow color developed immediately. This color is caused by new absorption bands which are not due to a chemical reaction but originate from the interaction in the ion pair. At concentrations above $\sim 10^{-4}$ M the ion pairing is complete since the new absorption obeys the Lambert–Beer law. The ion pair with M = Fe shows a well-resolved maximum at $\lambda = 418$ nm ($\epsilon = 88$) which is not obscured by absorptions of the separate complex ions. In the case of M = Ru and Os the new bands appear only as shoulders since the separate complex ions absorb in the same spectral region. However, in the difference spectra the new absorptions are clearly resolved: $\lambda_{max} = 332$ nm ($\epsilon = 78$) for M = Ru and $\lambda_{max} = 352$ nm ($\epsilon = 140$) for M = Os (Fig. 1).

It is suggested that these bands are assigned to outer-sphere MMCT transitions from the reducing metal centers M(II) to the oxidizing Pt(IV). When Fe is replaced by Os and Ru the MMCT band undergoes a blue shift in qualitative agreement with the expectation since the reducing strength decreases from $[Fe(CN)_6]^{4-}$ ($E_{1/2} = 0.19$ V *versus* SCE) to $[Os(CN)_6]^{4-}$ (0.40 V) and $[Ru(CN)_6]^{4-}$ (0.70 V) [1].

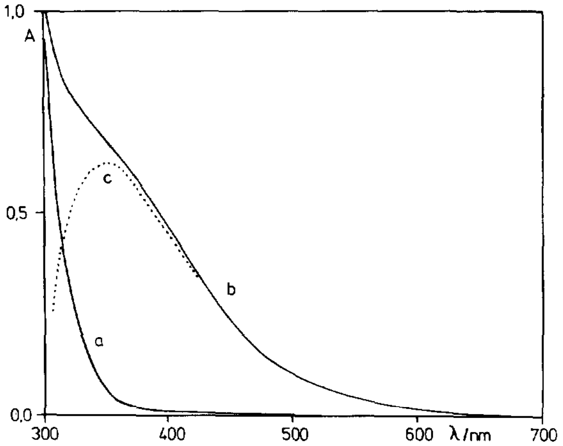

Fig. 1. Electronic absorption spectra of aqueous 10^{-2} M $[Pt(NH_3)_5Cl](ClO_4)_3$ and 10^{-2} M $K_4[Os(CN)_6]$ as separate solutions (a), as a mixture (b), and the difference spectrum (c = b – a); 298 K, 1-cm cell.

A new band was also observed in an aqueous solution of the ion pair $[Pt(NH_3)_5Cl]^{3+}[Pt(CN)_4]^{2-}$. The difference spectrum revealed an absorption at $\lambda_{max} = 295$ nm which is assigned to a MMCT transition from Pt(II) to Pt(IV).

These observations require some further comments. Optical MMCT transitions between weakly coupled redox centers can be evaluated on the basis of the Hush theory [9, 10]. The energy of the MMCT band ($\bar{\nu}_{max}$) is given by the simple equation: $\bar{\nu}_{max} = \Delta E + \chi$. The term ΔE is the difference of the potentials of both redox couples which are involved in the electron transfer process. The reorganizational energy χ is the sum of an inner-sphere (χ_i) and an outer-sphere (χ_o) contribution. The inner-sphere part depends largely on the extent of structural changes which are associated with the change of metal oxidation states. The outer-sphere contribution is determined by the solvent polarity and the distance between the redox centers.

On the first view the high energy of the MMCT bands of the ion pairs $[Pt(NH_3)_5Cl]^{3+}[M(CN)_6]^{4-}$ seems to be surprising since $[Pt(NH_3)_5Cl]^{3+}$ is an oxidant of moderate strength ($E_p = 0.24$ V *versus* NCE) [11]. However, the potentials of Pt(IV) complexes are generally known only for $2e^-$ reductions to Pt(II) while the optical MMCT transition as a one-electron process leads to Pt(III). Since Pt(III) does not exist as a stable oxidation state and may occur only as a high-energy intermediate Pt(IV) must be a very weak oxidant with regard to the

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*Author to whom correspondence should be addressed.

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Pt(IV)/(III) redox couple. It follows that ΔE of the ion pairs $[Pt(NH_3)_5Cl]^{3+}[M(CN)_6]^{4-}$ is certainly much larger than that which could be calculated from the experimental potentials. This may explain the high energy of these MMCT transitions at least partially. The reorganizational energy should be also important. Since $[Pt(NH_3)_5Cl]^{3+}$ is a pseudooctahedral d^6 complex the MMCT transition terminates in the antibonding e_g orbitals. The d^7 Pt(III) complex certainly undergoes a large distortion which requires a large reorganizational energy [12].

The MMCT band of the ion pair $[Pt(NH_3)_5Cl]^{3+}$-$[Pt(CN)_4]^{2-}$ appears at an energy which is even higher than those of $[Pt(NH_3)_5Cl]^{3+}[M(CN)_6]^{4-}$. In this case the MMCT transition from Pt(II) to Pt(IV) generates two Pt(III) centers. Again, Pt(IV) must be a very weak oxidant. In addition, Pt(II) is now also a very weak reductant with regard to the Pt(II)/(III) redox couple*. It follows that ΔE should be very large. The reorganizational energy must be also extremely large for this MMCT transition since in addition to the distortion which is associated with the reduction of Pt(IV) the oxidation of square-planar Pt(II) leads to considerable structural changes by the attachment of new ligands [12]. However, in Wolffram's red and related solid Pt(II)/(IV) mixed-valence compounds the MMCT bands appear at a rather long wavelength (~500 nm) [6]. This low energy may be due to two effects. In Wolffram's red Pt(II) is bridged perpendicular to its square plane by the halide ligands of octahedral Pt(IV). This structure which contains a Pt(II)...X–Pt(IV)–X...Pt^{II} chain may not require a very large energy for the MMCT transition. The reorganizational energy could be relatively small since the halide ligands of Pt(IV) are already rather close to Pt(II) prior to the MMCT transition. Since the aqueous ion pairs of Pt(IV) and Pt(II) are certainly not forced to any particular alignment the reorganizational energy of the Pt(II) to Pt(IV) MMCT transition can be very big. This energy as well as the large difference of the redox potentials ΔE may explain the occurrence of the MMCT band of the ion pair $[Pt(NH_3)_5Cl]^{3+}[Pt(CN)_4]^{2-}$ at a very short wavelength. These considerations are certainly also of importance with regard to the thermal electron exchange between Pt(IV) and Pt(II) [14].

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*In the presence of Cl^- the complex $[Pt^{II}(CN)_4]^{2-}$ is oxidized to $[Pt^{IV}(CN)_4Cl_2]$ at $E^\circ = 0.89$ V [13].