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# New donor–acceptor system based on $[Pt(NH_3)_4]^{2+}$ and $[W(CN)_8]^{3-}$ ions

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A new donor–acceptor system based on $[Pt(NH_3)_4]^{2+}$ and $[W(CN)_8]^{3-}$ has been characterized in aqueous solution and the solid state by spectroscopic and electrochemical techniques. In aqueous solution the 1 : 1 ion pair $\{[Pt(NH_3)_4]^{2+},[W(CN)_8]^{3-}\}$ exhibits an outer-sphere metal-to-metal charge-transfer transition at 485 nm ($\varepsilon = 49 \pm 2$ dm$^3$ mol$^{-1}$ cm$^{-1}$) with association constant $K_A = 26 \pm 3$ dm$^3$ mol$^{-1}$ at $I = 0.45$ mol dm$^{-3}$ ($KNO_3$) and 298 K. Electrochemical measurements revealed a $[W(CN)_8]^{3-/4-}$ reversible couple at +0.27 V (*vs.* saturated calomel electrode) in 0.1 mol dm$^{-3}$ $KNO_3$ for the novel ion pair. The $\{[Pt(NH_3)_4]^{2+},[W(CN)_8]^{3-}\}$ system is paramagnetic in aqueous solution ($g_{iso} = 1.96$ at 293 K). The results are interpreted using Hush theory (coupling parameters $\alpha^2 = 1.69 \times 10^{-4}$ and $H_{if} = 268$ cm$^{-1}$, reorganization energy for the optical electron-transfer process $\chi = 164.6$ kJ mol$^{-1}$, thermal activation barrier $E_{th} = 92.4$ kJ mol$^{-1}$ and electron-transfer rate constant $k_{et} = 3.3 \times 10^{-4}$ s$^{-1}$) and compared with the corresponding parameters for other $[M(CN)_n]^{3-/4-}$ couples. The bimetallic Pt–W system has been isolated in the solid state as $[Pt(NH_3)_4]_2[W(CN)_8][NO_3]\cdot 2H_2O$. The complex is paramagnetic (at 293 K $g_{iso} = 1.97$; at 77 K $g_\perp = 1.96$, $g_\parallel = 1.98$).

Redox couples of the cyano complexes of the transition metals are of continued interest in extensive studies of electron-transfer processes between metal centres in donor–acceptor systems consisting of both contact ion pairs and cyanide-bridged complexes.[1–10] While hexacyano complexes of Group 8 are widely employed as the donor moieties, relatively few systems involving donor octacyanometalates(IV) (M = Mo or W) in ion pairs[11,12] and in heterobinuclear dimers with pentaammine-osmium(III) acceptor sites[13] have been reported. Systems involving anionic electron acceptors are scarce[1–9] and, in the case of cyano complexes, are exclusively limited to $[Fe(CN)_6]^{3-}$.[14] It has recently been demonstrated[15–19] that the redox reactions of $[M(CN)_6]^{3-}$ (M = Fe, Ru or Os) and $[PtL_4]^{2+}$ (L = $NH_3$ or $\frac{1}{2}$ ethane-1,2-diamine) afford trinuclear, cyanide-bridged complex ions $[(NC)_5M^{II}{-}CN{-}Pt^{IV}L_4{-}NC{-}M^{II}(CN)_5]^{4-}$, the stoichiometry of which has been attributed to the one-electron nature of the $[M(CN)_6]^{3-/4-}$ couples along with the two-electron nature of the platinum redox potential.[18]

In the present paper the results of spectroscopic and electrochemical investigations of the new donor–acceptor system consisting of $[Pt(NH_3)_4]^{2+}$ and $[W(CN)_8]^{3-}$ in aqueous solution and the solid state are reported. The reaction of $[Pt(NH_3)_4]^{2+}$ with $[W(CN)_8]^{3-}$, unlike the $[M(CN)_6]^{3-}$ ions, generates the $\{[Pt(NH_3)_4]^{2+},[W(CN)_8]^{3-}\}$ ion pair in aqueous solution. The factors that influence the reactivity of the system and the magnitude of the electronic coupling are discussed and compared with data for other homoleptic cyano couples. The bimetallic Pt–W system in the solid state was isolated as the paramagnetic double salt $[Pt(NH_3)_4]_2[W(CN)_8][NO_3]\cdot 2H_2O$.

The present study of metal-to-metal charge-transfer phenomena between $[Pt(NH_3)_4]^{2+}$ and $[W(CN)_8]^{3-}$ increases the number of homoleptic cyano complexes systems for which Hush parameters are now available and provides further insights into electron-transfer processes.

## Experimental

### Materials

The compounds $K_3[W(CN)_8]\cdot 1.5H_2O$[20] and $K_4[W(CN)_8]\cdot 2H_2O$[21] were prepared according to the published procedures; $[Pt(NH_3)_4(NO_3)_2]$ was obtained from Aldrich and used without further purification. All other materials were of analytical grade (Aldrich) and used as supplied.

### Apparatus

The UV/VIS spectra were recorded on a Shimadzu 2101 PC spectrophotometer, diffuse reflectance spectra of solid samples as dispersions in $BaSO_4$ with a Shimadzu 2101 PC equipped with a Shimadzu ISR-260 integrating-sphere assembly using a $BaSO_4$ disc as the reference, infrared spectra from KBr pellets in the 4000–400 cm$^{-1}$ range on a Bruker IFS 47 instrument and ESR spectra on an ESR 220 X-band spectrometer at 9.5 GHz microwave frequency (298 K) in the range 0–500 mT. A model EA9 (MTM) multipurpose electrochemical analyser was employed for electrochemical measurements. A standard three-electrode configuration with a platinum working and counter electrode and a Ag–AgCl reference electrode were used. Thermogravimetric (TGA) and differential thermal (DTA) analyses were performed under argon on a Metler TG-2 thermoanalyser.

### Preparation of bis[tetraammineplatinum(II)] octacyanotungstate(V) nitrate dihydrate, $[Pt(NH_3)_4]_2[W(CN)_8][NO_3]\cdot 2H_2O$

Equimolar (0.10 mol dm$^{-3}$) aqueous solutions of $[Pt(NH_3)_4(NO_3)_2]$ and $K_3[W(CN)_8]\cdot 1.5H_2O$ were combined in 2 : 1 molar ratio, respectively. An orange precipitate formed immediately and was filtered out under vacuum, washed with distilled water and dried in air. Yield: 79% (Found: C, 9.75; H, 2.75; N, 22.95; $H_2O$, 3.0. Calc. for $C_8H_{28}N_{17}O_5W$: C, 9.45; H, 2.8; N, 23.45; $H_2O$, 3.55%).

The $[W(CN)_8]^{3-}$ solutions were protected from light by means of aluminium-covered containers. All manipulations and measurements were carried out in red light due to the photosensitivity of the tungsten(V) complex.[22]

## Results and Discussion

When a colourless aqueous solution of $[Pt(NH_3)_4(NO_3)_2]$ was mixed with a colourless aqueous solution of $K_3[W(CN)_8]$ the mixture turned reddish immediately. The electronic spectra of parent complexes and of the $[Pt(NH_3)_4]^{2+}$–$[W(CN)_8]^{3-}$ system

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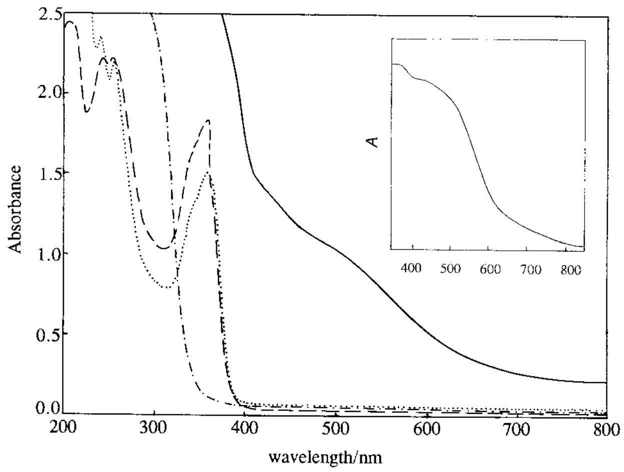

**Fig. 1** Electronic absorption spectra of aqueous 5 × $10^{-2}$ mol $dm^{-3}$ $[Pt(NH_3)_4][NO_3]_2$ (–•–•–), 1 × $10^{-3}$ mol $dm^{-3}$ $K_3[W(CN)_8]$ (– – – –) and equimolar mixtures of $[Pt(NH_3)_4][NO_3]_2$ and $K_3[W(CN)_8]$: 4 × $10^{-2}$ mol $dm^{-3}$ (——) and 8 × $10^{-4}$ mol $dm^{-3}$ (......) at $I = 0.45$ mol $dm^{-3}$ ($KNO_3$), $T = 298$ K. Inset: the diffuse reflectance spectrum of $[Pt(NH_3)_4]_2[W(CN)_8][NO_3]\cdot 2H_2O$

are given in Fig. 1. The spectrum of the mixture consists of a broad absorbance with two overlapping bands at λ 430 and 485 nm. On dilution the system shows higher-energy bands which are a simple addition of the $[W(CN)_8]^{3-}$ and $[Pt(NH_3)_4]^{2+}$ transitions. The band at 430 nm of the product appears in the same spectral region as the ligand-to-metal charge transfer (l.m.c.t.) $a_1$ ($d_{z^2}$) $\longleftarrow$ $b_2$ (σ) and ligand-field $a_1$ ($d_{z^2}$) $\longleftarrow$ $b_1$ ($d_{x^2-y^2}$) transitions for $[W(CN)_8]^{3-}$ and $[W(CN)_8]^{4-}$, respectively.[23–25] The new band centred at 485 nm can thus be assigned to the charge-transfer transition between the metal centres.

The room-temperature ESR spectrum of a 1:1 aqueous solution of $[Pt(NH_3)_4]^{2+}$ and $[W(CN)_8]^{3-}$ shows a signal at $g_{iso} = 1.96$. While the paramagnetic behaviour can be attributed to either a tungsten(V) ($d^1$)[26,27] or platinum(III) ($d^7$)[28] centre, the spectrum is characteristic of mononuclear $[W(CN)_8]^{3-}$ with $a(^{183}W) = 55.6$ G (5.56 × $10^{-3}$ T). The ESR experiment indicates that two-electron oxidation of $[Pt(NH_3)_4]^{2+}$ by $[W(CN)_8]^{3-}$ leading to a hypothetical trimeric $W^{IV}Pt^{IV}W^{IV}$ cyano-bridged species does not occur. The system appears to be controlled by the ability of the $[W(CN)_8]^{3-}$ ion to supply the cyano bridge, according to the requirements of the inner-sphere mechanism of oxidation of $Pt^{II}$ to $Pt^{IV}$. The square-antiprismatic $D_{4d}$ $[W(CN)_8]^{3-}$ complex creates a large barrier to this process.

Cyclic voltammograms carried out in 0.1 mol $dm^{-3}$ $KNO_3$ by using platinum working and counter electrodes show a quasi-reversible isolated $[W(CN)_8]^{3-/4-}$ redox couple with $E_{\frac{1}{2}} = +0.27$ V *versus* saturated calomel electrode (SCE) and a 60 mV peak-to-peak separation.[29] This result indicates the formation of a donor–acceptor ion pair, consisting of the parent complex ions $\{[Pt^{II}(NH_3)_4]^{2+}, [W^{V}(CN)_8]^{3-}\}$ in aqueous solution, according to equation (1). The association constant $K_A$ and molar

$$[Pt(NH_3)_4]^{2+} + [W(CN)_8]^{3-} \overset{K_A}{\rightleftharpoons} \{[Pt(NH_3)_4]^{2+},[W(CN)_8]^{3-}\} \quad (1)$$

absorption coefficient $\varepsilon_{485}$ of the ion pair were determined spectrophotometrically. The dependence of the absorbance $A_i$ of the system at λ 485 nm on the equimolar concentration of the species involved $\{[Pt(NH_3)_4{}^{2+}]_{total} = [W(CN)_8{}^{3-}]_{total} = c_{tot}\}$ is shown in Fig. 2. The absorbance $A_i$ of the system may be written as in equation (2), where $\varepsilon_{Pt}$, $\varepsilon_W$ and $\varepsilon_{IP}$ are the molar

$$A_i = \varepsilon_{Pt}(c_{tot} - c_{IP}) + \varepsilon_W(c_{tot} - c_{IP}) + \varepsilon_{IP}c_{IP} \quad (2)$$

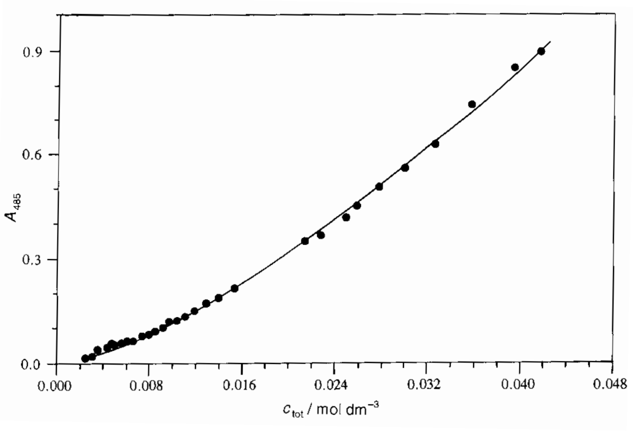

**Fig. 2** Dependence of the absorbance $A_{485}$ on the equimolar concentration $c_{tot}$ of $[Pt(NH_3)_4]^{2+}$ and $[W(CN)_8]^{3-}$, $I = 0.45$ mol $dm^{-3}$ ($KNO_3$), $T = 298$ K, optical path 1.0 cm. The solid line represents the non-linear least-squares fitting of the data to equation (4)

absorption coefficients of $[Pt(NH_3)_4]^{2+}$, $[W(CN)_8]^{3-}$ and $\{[Pt(NH_3)_4]^{2+}, [W(CN)_8]^{3-}\}$, respectively, whereas $(c_{tot} - c_{IP})$ and $c_{IP}$ are the concentrations of the free ions and ion pair, respectively. Combination of equation (2) and the expression for the concentration of the ion pair derived from the association constant $K_A$ for the 1:1 ion pair [equation (3)], gives expression (4) for the dependence of the absorbance $A_i$ of the

$$K_A = c_{IP}/(c_{tot} - c_{IP})^2 \quad (3)$$

$$A_i = \varepsilon_s c_{tot} + (\varepsilon_{IP} - \varepsilon_s)[1 + 2K_A c_{tot} - (1 + 4K_A c_{tot})^{\frac{1}{2}}]/2K_A \quad (4)$$

system on the concentration $c_{tot}$, where $\varepsilon_s$ is the sum of the molar absorption coefficients of $[Pt(NH_3)_4]^{2+}$ and $[W(CN)_8]^{3-}$. From a non-linear least-squares fit of the absorbance data using equation (4) the values of $\varepsilon_{IP}$ at 485 nm and $K_A$ are estimated to be 49 ± 2 $dm^3$ $mol^{-1}$ $cm^{-1}$ and 26 ± 3 $dm^3$ $mol^{-1}$, respectively at $I = 0.45$ mol $dm^{-3}$ and 298 K.

The properties of the metal-to-metal charge-transfer transition [equation (5)] have been tested according to Hush theory,[30]

$$\{[Pt^{II}(NH_3)_4]^{2+},[W^{V}(CN)_8]^{3-}\} \xrightarrow{h\nu} \{[Pt^{III}(NH_3)_4]^{3+},[W^{IV}(CN)_8]^{4-}\} \quad (5)$$

which relate optically induced charge transfer and thermal electron transfer. The extent of charge delocalization between $[Pt(NH_3)_4]^{2+}$ and $[W(CN)_8]^{3-}$ within the contact ion pair is described by the parameters $\alpha^2$ and $H_{if}$ as defined by equations (6) and (7), respectively. The $Pt^{II}$→$W^{V}$ metal-to-metal charge-

$$\alpha^2 = 4.24 \times 10^{-4}\varepsilon_{max}\Delta\nu_{\frac{1}{2}}/(\nu_{max}r^2) \quad (6)$$

$$H_{if}/cm^{-1} = \nu_{max}\alpha = 2.05 \times 10^{-2}(\varepsilon_{max}\Delta\nu_{\frac{1}{2}}\nu_{max})^{\frac{1}{2}}/r \quad (7)$$

transfer (m.m.c.t.) transition occurs at ν 20 618 $cm^{-1}$ with a bandwidth at half-maximum $\Delta\nu_{\frac{1}{2}} = 7194$ $cm^{-1}$, determined by doubling the half-bandwidth on the low-energy side. The intermetallic distance of closest approach $r = 6.55$ Å has been calculated as the average statistical geometric distance between the donor and acceptor sites. Two limiting geometric orientations have been taken into account. The first model consists of the square plane of $[Pt(NH_3)_4]^{2+}$ at the van der Waals contact with the nitrogen of the cyanide ligand of the $[W(CN)_8]^{3-}$ complex. The second assumes that the ammine ligand of $[Pt(NH_3)_4]^{2+}$ is within hydrogen-bonding distance of the nitrogen of the cyano group of $[W(CN)_8]^{3-}$. The distances have been calculated on the basis of crystallographic data.[15,31] The

**Table 1** Selected infrared bands ($cm^{-1}$) and their assignments for $[Pt(NH_3)_4]_2[W(CN)_8][NO_3]\cdot 2H_2O$ and related compounds

| Assignment | $[Pt(NH_3)_4]_2[W(CN)_8][NO_3]\cdot 2H_2O$ | $[Pt(NH_3)_4(NO_3)_2]$ | $[Pt(NH_3)_6Cl_4]$* | $K_4[W(CN)_8]\cdot 2H_2O$ | $K_3[W(CN)_8]\cdot 1.5H_2O$ | $KNO_3$ |
|---|---|---|---|---|---|---|
| $\nu_{asym}(NH_3)$ | 3292vw, 3116vw | 3282vw, 3219vw | 3150 | | | |
| $\nu(CN)$ | 2138vw, 2129w, 2124m, 2113s, 2098vs, 2071vw, 2057vw | | | 2138w, 2130m, 2124m, 2101 (sh), 2096vs, 2055vw | 2162w, 2159m, 2151vs, 2148vs, 2142vs, 2138m | |
| $\nu(NO_3)$ | 1384vs | 1366vs | | | | 1383vs |
| $\delta(NH_3)$ | 1619w, 1340s | 1588w, 1325vs | 1370 | | | |
| $\rho_r(NH_3)$ | 840m, 833vw | 856m | 950 | | | |
| $\pi(NO_3)$ | 826vw | 823m | | | | 827m |
| $\nu(PtN)$ | 541vw, 516vw | 505w | 530, 516 | | | |
| $\nu(WC)$ | 487m, 481m, 471w | | | 486s, 468s, 406s | 562s, 442s, 402m | |

* Ref. 16.

calculated extent of delocalization of the electron between the donor and acceptor, $\alpha^2 = 1.69 \times 10^{-4}$, indicates that the $\{[Pt^{II}(NH_3)_4]^{2+},[W^V(CN)_8]^{3-}\}$ ion pair is a Robin and Day[32] Class II species. The value of the electron-exchange matrix element $H_{if} = 268$ $cm^{-1}$ indicates that the electron-transfer reaction in the optical ion-pair configuration is in the adiabatic regime. These values of $\alpha^2$ and $H_{if}$ fall within the nearly metal-independent range found for ion pairs and electronically weakly coupled ligand-bridged dimers.[1–9] The Hush relationship between the optical electron-transfer energy and thermal activation parameters is given by equation (8), where $E_{op}$ is the

$$E_{op} = \chi + \Delta E \qquad (8)$$

energy of the m.m.c.t. transition and $\chi$ is the reorganization energy. The term $\Delta E$ represents the degree of electronic asymmetry and is the free energy for the related thermal redox reaction (9). It can be estimated from the formal redox potential of the redox couples involved, $\Delta E = E_{\frac{1}{2}}[W(CN)_8{}^{3-/4-}] - E_{\frac{1}{2}}[Pt(NH_3)_4{}^{3+/2+}]$. The one-electron redox potential $E_{\frac{1}{2}}[Pt(NH_3)_4{}^{3+/2+}] = 1.12$ V *vs.* SCE has been estimated on the basis of a Latimer diagram from the known overall two-electron redox potential of the $[Pt(NH_3)_6]^{4+}$–$[Pt(NH_3)_4]^{2+}$ couple (0.16 V *vs.* SCE) and the one-electron redox potential of the $[Pt(NH_3)_6]^{4+/3+}$ couple (−0.80 V *vs.* SCE).[18] For the ion pair $\{[Pt^{II}(NH_3)_4]^{2+},[W^V(CN)_8]^{3-}\}$ the calculated difference in redox potentials is $\Delta E = 82$ kJ $mol^{-1}$. The reorganization energy $\chi$ for this ion pair, as determined from equation (8), was found to be 164.6 kJ $mol^{-1}$. This value is in the range 155–171.5 kJ $mol^{-1}$ found for the aqueous ion pairs $\{[Os(NH_3)_5Cl]^{2+},[M(CN)_6]^{4-}\}$[5–7] and close to that for the trimeric species $[L(NC)_4Fe^{II}\text{–}CN\text{–}Pt^{IV}(NH_3)_4\text{–}NC\text{–}Fe^{II}(CN)_4L]^{4-}$ (L = CN or substituted N-aromatic ligand).[17,18] The inner-sphere contribution $\chi_i$ to the reorganization energy $\chi$ depends on the oxidation state-dependent metal–ligand bond lengths and angles in the $[Pt(NH_3)_4]^{2+/3+}$ and $[W(CN)_8]^{3-/4-}$ couples. For the octacyanotungstate couple the very small tungsten–cyanide bond length and angle variations with oxidation state,[33] consistent with the weakly bonding highest occupied molecular orbital (HOMO) $d^1{}_{z^2}$ in $[W(CN)_8]^{3-}$ of $D_{4d}$ symmetry and $d^2{}_{x^2-y^2}$ in $[W(CN)_8]^{4-}$ of $D_{2d}$ symmetry,[23,24,34] do not contribute significantly to the $\chi_i$ value. A large contribution to the reorganization energy is expected for the $[Pt(NH_3)_4]^{2+/3+}$ couple involving significant geometrical distortion from low-spin square-planar $d^8$ to the $d^7$ system upon electron transfer from the $d_{xy}$ orbital of $Pt^{II}$ to the $d_{z^2}$ in $[W(CN)_8]^{3-}$. Accordingly, a reorganization of the solvent environment, reflected in the $\chi_o$ contribution to the reorganization energy $\chi$, is associated with the $[Pt(NH_3)_4]^{2+/3+}$ couple. Based on the determined $E_{op}$ and $\Delta E$ values, the theoretical bandwidth at half-maximum $\Delta\nu_{\frac{1}{2}}$(theor) calculated by equation (10) is found to be 5638 $cm^{-1}$. Therefore $\Delta\nu_{\frac{1}{2}}/\Delta\nu_{\frac{1}{2}}$(theor) = 1.3,

$$\{[Pt^{II}(NH_3)_4]^{2+},[W^V(CN)_8]^{3-}\} \longrightarrow \{[Pt^{III}(NH_3)_4]^{3+},[W^{IV}(CN)_8]^{4-}\} \qquad (9)$$

$$\Delta\nu_{\frac{1}{2}}(\text{theor}) = [2310(E_{op} - \Delta E)]^{\frac{1}{2}} \qquad (10)$$

which is not unexpected due to the unharmonicity and other effects.[1–6] The barrier to thermal electron transfer $E_{th}$ calculated according to equation (11) is found to be 92.4 kJ $mol^{-1}$, which is

$$E_{th} = E_{op}{}^2/4\chi \qquad (11)$$

the typical value for ion pairs.[1–9] The rate constant $k_{et}$ for the thermal electron-transfer process[35] [equation (9)] can be expressed as in equation (12), where $\kappa_{el}$ is the electronic

$$k = \kappa_{el}\nu_n \exp(-\Delta G^{\ddagger}/RT) \qquad (12)$$

transmission coefficient and is approximately one for an adiabatic electron transfer, $\nu_n$ is the effective nuclear vibration frequency that destroys the activated complex configuration and is ≈$5 \times 10^{12}$ $s^{-1}$ and $\Delta G^{\ddagger}$ is the thermal activation free energy (approximately $E_{th}$). The calculated relatively slow rate constant $k = 3.3 \times 10^{-4}$ $s^{-1}$ appears to be controlled by the large value of the reorganization energy $\chi$. Fig. 3 relates the electronic parameters discussed, depicting the electron-transfer process in terms of potential-energy surfaces for the $\{[Pt^{II}(NH_3)_4]^{2+},[W^V(CN)_8]^{3-}\}$ ion pair and its redox isomer $\{[Pt^{III}(NH_3)_4]^{3+},[W^{IV}(CN)_8]^{4-}\}$.

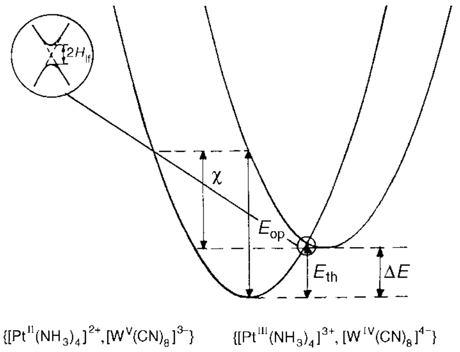

**Fig. 3** Schematic representation of the potential energy diagram of the $\{[Pt^{II}(NH_3)_4]^{2+},[W^V(CN)_8]^{3-}\}$ ion pair including the optical m.m.c.t. transition. For description see text

The bimetallic Pt–W system has been isolated in the solid state as $[Pt(NH_3)_4]_2[W(CN)_8][NO_3]\cdot 2H_2O$ by mixing $[Pt(NH_3)_4(NO_3)_2]$ and $K_3[W(CN)_8]\cdot 1.5H_2O$ in aqueous solution in a 2 : 1 molar ratio. This orange solid appeared to be insoluble in water and other common polar solvents. The inset in Fig. 1 shows the diffuse reflectance spectrum of the crystalline complex. The correspondence of the absorption and diffuse reflectance spectra indicates the similarity of $\{[Pt(NH_3)_4]^{2+}$, $[W(CN)_8]^{3-}\}$ in aqueous solution to $[Pt(NH_3)_4]_2[W(CN)_8][NO_3]\cdot 2H_2O$ in the solid state. The solid species is paramagnetic and shows an ESR signal typical of $[W(CN)_8]^{3-}$ ion with $g_{iso} = 1.97$ at 293 K, $g_{\perp} = 1.96$ and $g_{\parallel} = 1.98$ at 77 K.[25,26] The ESR data suggest a tungsten(V) oxidation state in $[Pt(NH_3)_4]_2[W(CN)_8][NO_3]\cdot 2H_2O$. The infrared data are presented in Table 1 and assigned by analogy with previously reported complexes.[16,26,36] A comparison of the data indicates that the ν(CN) and ν(WC) frequencies of $[Pt(NH_3)_4]_2[W(CN)_8][NO_3]\cdot 2H_2O$ resemble those of octacyanotungstate(IV) ion of $D_{2d}$ symmetry. It should be pointed out that the cyanide stretching transitions of $[W(CN)_8]^{4-}$ are much more intense than those of $[W(CN)_8]^{3-}$ and in the presence of the tungsten(IV) centre the characteristic frequencies of $W^V$ are completely suppressed. While the ammine infrared bands $\delta(NH_3)$ and $\nu_{asym}(NH_3)$ are similar to those of $[Pt(NH_3)_4(NO_3)_2]$, ν(PtN) is essentially the same as for $[Pt(NH_3)_6Cl_4]$. Moreover, the $\rho_r(NH_3)$ region contains bands corresponding to $Pt^{II}$ and $Pt^{IV}$. The infrared spectrum of $[Pt(NH_3)_4]_2[W(CN)_8][NO_3]\cdot 2H_2O$ indicates that the $[Pt(NH_3)_4]^{2+}$–$[W(CN)_8]^{3-}$ interaction in the solid state forces to some extent electron transfer from the platinum donor to the tungsten acceptor.

## Conclusion

The $[W(CN)_8]^{3-}$ ion is employed for the first time as the anionic electron acceptor in a new outer-sphere ion pair $\{[Pt(NH_3)_4]^{2+},[W(CN)_8]^{3-}\}$. The Hush model used to discuss the properties of the metal-to-metal charge-transfer transition of this ion pair and kinetic and thermodynamic factors for the corresponding thermal electron-transfer process confirms the nearly metal-independent coupling parameters, characteristic of outer-sphere ion pairs and electronically weakly coupled bridged dimers. The bimetallic Pt–W system has been isolated in the solid state as $[Pt^{II}(NH_3)_4]_2[W^V(CN)_8][NO_3]\cdot 2H_2O$. The $[Pt(NH_3)_4]^{2+}$–$[W(CN)_8]^{3-}$ system failed to give the hypothetical trimeric $W^{IV}Pt^{IV}W^{IV}$ cyano-bridged species in a two-electron redox process. The system appears to be controlled not only by the one-electron nature of the $[W(CN)_8]^{3-/4-}$ couple along with the two-electron nature of the platinum redox potential, but also by the ability of $[W(CN)_8]^{3-}$ ion to supply the cyano bridge, according to the requirements of the inner-sphere mechanism of the oxidation of $Pt^{II}$ to $Pt^{IV}$. The square-antiprismatic $D_{4d}$ $[W(CN)_8]^{3-}$ complex creates a large barrier to this process.

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