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Ion-pairing and charge-transfer interactions between octacyanomolybdates(IV) and -tungstates(IV) and diquaternary bipyridines

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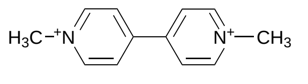
New salts of formula $[pq]_2[M(CN)_8]$ [M = Mo or W, pq = paraquat (1,1′-dimethyl-4,4′-bipyridinediium)] have been synthesized. The systems $\{A^{2+}, M(CN)_8{}^{4-}\}$ where A^{2+} = pq or dq (diquat, 6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium), which show optical electron transfer from anion to cation, were studied. The first association constants in aqueous solution were determined spectroscopically and the properties of the ion-pair charge-transfer bands were used for calculation of the thermodynamic parameters of the electron transfer and construction of potential-energy curves on the basis of the Hush model.

Photoinduced electron-transfer reactions are a subject of continuing interest. Electron transfer may cause drastic changes in the chemical behaviour of the acceptor and donor as it influences the redox and acid–base properties, kinetic stability and catalytic activity, which can lead to the formation of permanent photoproducts. Such processes may be employed in catalytic organic synthesis, solar-energy conversion or design of unconventional information-storage materials.

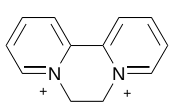
Ion pairs consisting of a redox donor and acceptor are particularly suitable for the investigation of intermolecular charge-transfer processes.[1] The properties of such systems can be easily tuned by modifications of the components. A variety of ion pairs formed by complex ions show optical charge transfer, which in many cases is connected with the presence of a new band in the visible region of the electronic spectrum. There are several known systems based on cobalt(III), ruthenium(III) and osmium(III) complexes as acceptors and ruthenium(II), osmium(II) and iron(II) complexes as donors. Similar behaviour is also shown by redox-active organic species.

In the course of our study on charge-transfer ion pairs we have investigated systems derived from octacyanometalates(IV) (M = Mo or W), which are reversible electron donors, and various polypyridinium cations. Salts of formulae $[Hbpy]_3[H_3O][M(CN)_8]\cdot 2H_2O$ (bpy = 2,2′-bipyridine)[2] and $[4,4'\text{-}H_2bpy]_2[M(CN)_8]\cdot 4.5H_2O$ (4,4′-bpy = 4,4′-bipyridine)[3] exhibit ion-pair charge-transfer (IPCT) bands in the region 400–600 nm both in the solid state and in aqueous solution. In addition to the optical effect the salt $[H_2bpy]_2[W(CN)_8]\cdot 4H_2O$,[4] quite unexpectedly, also shows significant thermal electron transfer in the solid state, which was detected in ESR measurements.

Recently we have extended our study to paraquat (pq = 1,1′-dimethyl-4,4′-bipyridinediium) and diquat (dq = 6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium) dications. The paraquat cation due to its low reversible reduction potential is widely used as a redox indicator (methyl viologen) and was employed in the majority of working photochemical water-reduction systems.[5,6] Diquat also forms a relatively stable radical monoanion, however its photoredox behaviour is much less studied than that of paraquat and there are only a few reports on charge-transfer ion pairs with diquat as an acceptor.[7] In this paper we report on the electron transfer in $\{A^{2+}, [M(CN)_8]^{4-}\}$ systems (A^{2+} = pq or dq).



pq



dq

Experimental

Materials

The initial molybdenum(IV) and tungsten(IV) complexes $K_4[M(CN)_8]\cdot 2H_2O$ were synthesized by methods described in the literature.[8,9] The aqueous solutions of acids $H_4[M(CN)_8]$ were obtained from potassium salts using ion-exchange technique (IR 120 ion-exchange resin in H^+ form).[10] 1,1′-Dimethyl-4,4′-bibipyridinediium dichloride hydrate (BDH Chemicals, UK) and other reagents and solvents of analytical grade (POCh, Poland) were used as supplied.

Syntheses

Bis(1,1′-dimethyl-4,4′-bipyridinediium) octacyanomolybdate(IV) $[pq]_2[Mo(CN)_8]$ 1. The salt $[pq]Cl_2\cdot H_2O$ (2.35 mmol, 0.646 g) was dissolved in an aqueous solution (100 cm^3) containing $H_4[Mo(CN)_8]$ (1.28 mmol, 0.394 g) and then acetone (300 cm^3) was carefully added to form a separate top layer. The mixture was allowed to stand for 3 d at room temperature. The resulting precipitate was filtered off, washed with water–acetone (1:2) and dried in air *via* suction. Yield: 0.541 g (68.1%) (Found: C, 57.17; H, 4.35; N, 25.17; H_2O, 0.0. Calc. for $C_{32}H_{28}MoN_{12}$: C, 56.89; H, 4.10; N, 24.85; H_2O, 0.0%). Selected IR absorption bands (cm^{-1}): 1350m, 1454m, 1510s, 1640vs (pq); 2098vs, 2105 (sh), 2118vw [ν(C≡N)].

Bis(1,1′-dimethyl-4,4′-bipyridinediium) octacyanotungstate(IV), $[pq]_2[W(CN)_8]$ 2. The salt was obtained in a similar way to **1**, except that $H_4[W(CN)_8]$ (1.28 mmol, 0.521 g) was used instead of the molybdenum compound. Yield: 0.567 g (63.2%) (Found: C, 50.18; H, 3.90; N, 22.22; H_2O, 0.0. Calc. for $C_{32}H_{28}N_{12}W$: C, 50.26; H, 3.66; N, 21.99; H_2O, 0.0%). Selected IR absorption bands (cm^{-1}): 1350m, 1452m, 1510m, 1640vs (pq); 2093vs, 2103 (sh), 2120vw [ν(C≡N)].

The salts $[dq]_2[Mo(CN)_8]\cdot 5H_2O$ **3** and $[dq]_2[W(CN)_8]\cdot 5H_2O$ **4** were prepared in a similar way. Their structure and solid-state properties will be reported separately.[11]

Analytical methods and physical measurements

Carbon, nitrogen and hydrogen were determined by organic microanalysis. The content of water was determined thermogravimetrically (TG). These analyses and differential thermal analysis (DTA) were performed under argon within the temperature range 25–400 °C, with a heating rate of 2.5 °C min^{-1} on a Mettler thermoanalyser. The UV/VIS absorption

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(Shimadzu 2101PC spectrometer) and UV/VIS/NIR reflectance spectra (Shimadzu 2101PC with ISR-260 device and Shimadzu 3101PC spectrometer) were recorded in the normal manner at 25 °C, and ESR spectra (Se/X-25, Poland) at room temperature. The number of paramagnetic centres was determined by comparison with $VO(SO_4)$ as standard. Infrared spectra were measured in KBr pellets on a Brüker IFS 48 spectrometer.

Determination of association constants

The association constants were determined spectrophotometrically by monitoring the absorbance of an aqueous solution of the cation and anion in 1 : 1 ratio at different concentrations. The measurements were performed at 25 °C with $d = 1$ cm at the wavelengths $\lambda = 525$ ($\nu = 19\,050$) (pq^{2+}, $Mo(CN)_8^{4-}$), 571 (17 500), (pq^{2+}, $W(CN)_8^{4-}$, 545 (18 350) (dq^{2+}, $Mo(CN)_8^{4-}$) and 625 nm (16 000 cm^{-1}) (dq^{2+}, $W(CN)_8^{4-}$). The ionic strength was adjusted to $I = 0.3$ mol dm^{-3} by addition of KCl (pq) or KBr (dq). Assuming equilibrium (1) the association constant can be expressed by

$$A^{2+} + M(CN)_8^{4-} \overset{K}{\rightleftharpoons} \{A^{2+},M(CN)_8^{4-}\} \qquad (1)$$

equation (2), where c_0 is the initial concentration of ions and

$$K = \frac{c_{ip}}{(c_0 - c_{ip})^2} \qquad (2)$$

c_{ip} is the concentration of ion pair in equilibrium. The measured absorbance A_m is represented by equation (3), where

$$A_m = \varepsilon_0(c_0 - c_{ip})d + \varepsilon c_{ip}d \qquad (3)$$

ε and ε_0 are the molar absorption coefficients at λ_{max} of the ion pair and of $M(CN)_8^{4-}$ ion {as determined for $K_4[M(CN)_8]$}. Combination of equations (2) and (3) gives expression (4) for K. The K and ε values were calculated simultaneously using

$$K = \frac{[(A_m/d) - \varepsilon c_0]/(\varepsilon - \varepsilon_0)}{\{c_0 - [(A_m/d) - \varepsilon_0 c_0]/(\varepsilon - \varepsilon_0)\}^2} \qquad (4)$$

the gradient method of function minimization (Fortran 77, routine FRPRMN).[12]

Results and Discussion

Ion pairing in solution

When a colourless aqueous solution of paraquat or diquat dihalide is added to a yellow solution of $H_4[M(CN)_8]$ the colour changes to brownish red (molybdenum complexes) or green (tungsten complexes). New absorption bands, which are IPCT in character, arise at 502 **1**, 571 **2**, 545 **3** and 625 nm **4** (Fig. 1). The energy of the optical electron transfer E_{op} is equal to 235, 208, 219 and 191 kJ mol^{-1} respectively. The bandwidths at half-maximum, $\Delta\nu_{\frac{1}{2}}$ (Table 1), are close to those observed for similar systems, *e.g.* pq^{2+}, $Fe(CN)_6^{4-}$ (6800 cm^{-1}[13]).

As expected for the absorbance of an ion pair the intensity of this band does not obey the Lambert–Beer law. We assumed that only the equilibrium (1) occurs. To minimize the formation of higher associates a 1 : 1 ratio of ions was used. Typical changes in absorbance are presented in Fig. 2.

The calculated association constants (Table 1), which depend mainly on the charges and radii of the ions, are practically the same for all four ion pairs. The molar absorption coefficients lie within the same range. We compared our systems with a related, widely studied ion pair {pq^{2+}, $Fe(CN)_6^{4-}$} which, due to identical charges and similar ionic radii, should have comparable association constants. The values obtained by Toma[14] ($\varepsilon = 150$–200 dm^3 mol^{-1} cm^{-1}, $K = 30$–40 dm^3 mol^{-1}) are indeed close, but estimates made by Meyer and co-workers[13] ($\varepsilon = 50$ dm^3 mol^{-1} cm^{-1}, $K = 190$–250 dm^3 mol^{-1}) significantly differ from our results. This discrepancy arises mostly from different methods of calculation. Meyer and co-workers used the method of independent estimation of ε directly from the absorption of the ion-pair solution at high concentrations assuming complete association, which however mathematically simpler gives inadequate results for systems with low association constants.

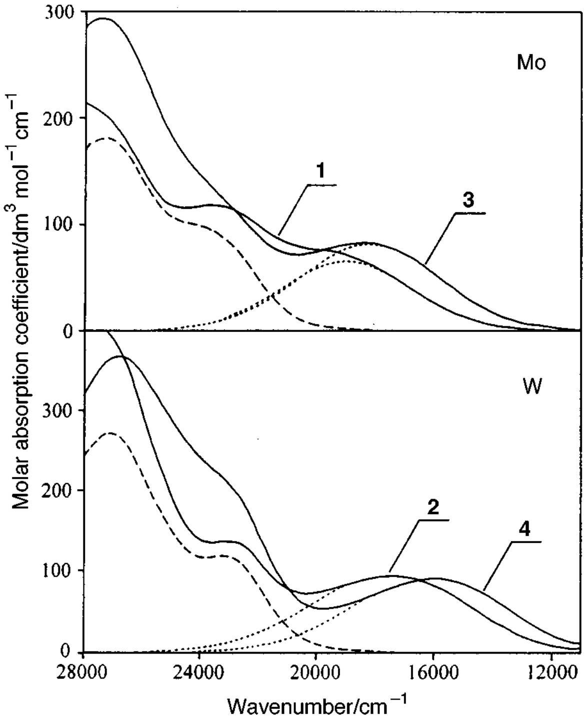


Fig. 1 Electronic absorption spectra in aqueous solutions of $[pq]_2[Mo(CN)_8]$ **1**, $[pq]_2[W(CN)_8]$ **2**, $[dq]_2[Mo(CN)_8]\cdot 5H_2O$ **3** and $[dq]_2[W(CN)_8]\cdot 5H_2O$ **4** (solid lines) with Gaussian profiles marked for IPCT bands (dotted lines). For comparison respective $K_4[M(CN)_8]\cdot 2H_2O$ spectra are presented (broken lines)

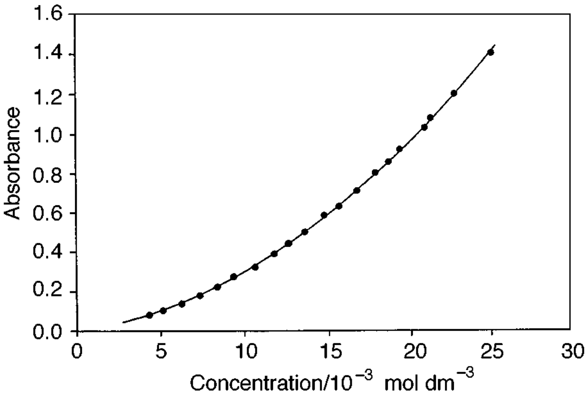


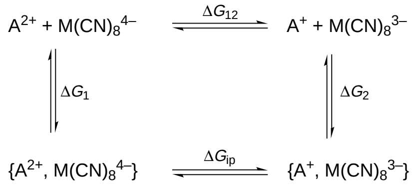
Fig. 2 Concentration dependence of the absorbance for an equimolar aqueous solution of dq and $[M(CN)_8]^{4-}$

Thermodynamics of electron transfer

In order to obtain quantitative information on non-spontaneous electron transfer in the systems studied we employed Hush theory.[15] The free-energy change associated with the electron transfer within the ion pair, ΔG_{ip}, can be calculated from the thermodynamic cycle presented in Scheme 1 as the sum of free energy changes of three processes: outer-sphere electron transfer from $M(CN)_8^{4-}$ to A^{2+} (ΔG_{12}), dissociation of {A^{2+}, $M(CN)_8^{4-}$} ion pair ($-\Delta G_1$) and association of A^+ and $M(CN)_8^{3-}$ ions (ΔG_2), equation (5).

Table 1 Thermodynamic parameters calculated for $\{A^{2+}, M(CN)_8^{4-}\}$ systems in aqueous solutions

Ion pair	d/Å	ν_{max}/ cm^{-1}	$\Delta\nu_{\frac{1}{2}}$/ cm^{-1}	ε_{max}/dm^3 mol^{-1} cm^{-1}	K/dm^3 mol^{-1}	ΔG_1/kJ mol^{-1}	$\Delta G_{1\ calc}$/ kJ mol^{-1}	ΔG_2/kJ mol^{-1}	ΔG_{12}/kJ mol^{-1}	E_{op}/kJ mol^{-1}	ΔE/kJ mol^{-1}	E_a/kJ mol^{-1}
pq^{2+}, $Mo(CN)_8^{4-}$	7.49	19 700	6100	175	19	−7.3	−7.9	−3.0	119	235	123	123
pq^{2+}, $W(CN)_8^{4-}$	7.49	17 400	6500	190	23	−7.8	−7.9	−3.0	93	208	97	98
dq^{2+}, $Mo(CN)_8^{4-}$	7.45	18 300	6600	195	21	−7.5	−7.9	−3.0	110	219	115	115
dq^{2+}, $W(CN)_8^{4-}$	7.45	16 000	6800	255	22	−7.7	−7.9	−3.0	84	191	89	89



Scheme 1 Thermodynamic cycle for calculation of the free energy of electron transfer within the ion pair

$$\Delta G_{ip} = \Delta G_{12} - \Delta G_1 + \Delta G_2 \tag{5}$$

The calculated thermodynamic parameters are listed in Table 1. The ΔG_{12} values can be easily obtained from redox potentials of the ions: $E_{\frac{1}{2}} = 0.78$ $[Mo(CN)_8^{3-/4-}]$, 0.51 $[W(CN)_8^{3-/4-}]$,[2] −0.45 ($pq^{2+/+}$)[13] and −0.36 V ($dq^{2+/+}$).[16] The value of ΔG_1 was determined from experimental association constants K. The value of ΔG_2 cannot be obtained experimentally so we used values calculated from the Eigen–Fuoss equation (6), where z_1

$$\Delta G^A = \frac{z_1 z_2 e^2}{4\pi\varepsilon d}\cdot\frac{1}{1+\kappa d} - RT\ln\frac{4000\pi N_A d^3}{3} \tag{6}$$

and z_2 are the charges of the ions, e is the charge of the electron (C), ε the relative permittivity of water, κ the Debye inverse length (1.80×10^7 cm^{-1} for $I = 0.3$ mol dm^{-3}) and N_A is Avogadro's number. The hard-sphere contact distances d (m) between reacting ions were calculated as the sum of ionic radii. The $M(CN)_8^{4-}$ radius (4.8×10^{-10} m for Mo and W) was calculated from the crystal structures of **3** and **4**[11] and the nitrogen van der Waals radius.[17] The pq^{2+} and dq^{2+} radii, calculated from the volume increments,[17] are between 1.70×10^{-10} and 3.56×10^{-10} (pq) and 1.70×10^{-10} and 3.49×10^{-10} m (dq). For calculations we have taken the average values of 2.63×10^{-10} and 2.60×10^{-10} m respectively. Since the interreactant distances cannot be precisely estimated, there is a possibility of wrong evaluation of association free energies. To avoid this problem we also estimated $\Delta G_{1\ calc}$. Comparison between calculated and experimental ΔG_1 energies shows that the adopted d values give reasonably good results. Since the association free energies are small compared to the free energy of electron transfer ΔG_{12}, the ΔG_{ip} value is practically not affected by the interionic distance estimations. Assuming that the entropy change is negligible,[7] ΔG_{ip} is considered equal to ΔH_{ip}, and in absence of pressure–volume work $\Delta H_{ip} = \Delta E$ (the external energy change in the system). Finally the activation energy for the process was estimated from relation (7) where the reorganization energy, $\chi = E_{op} - \Delta E$.

$$E_a = E_{op}^2/4\chi \tag{7}$$

The potential-energy diagram for $\{A^{2+}, M(CN)_8^{4-}\}$ systems is presented in Fig. 3. The striking feature of the thermodynamics of the systems studied is the low activation energy of electron transfer, which is almost equal to the energy difference ΔE. Consequently, the energy barrier for back electron transfer practically does not exist, and therefore the relaxation of the charge transfer state is very quick. Such a phenomenon was previously observed for other systems[7,13] and together with the high charge of the reactants it indicates that a photoredox process leading to permanent products is unlikely to occur.

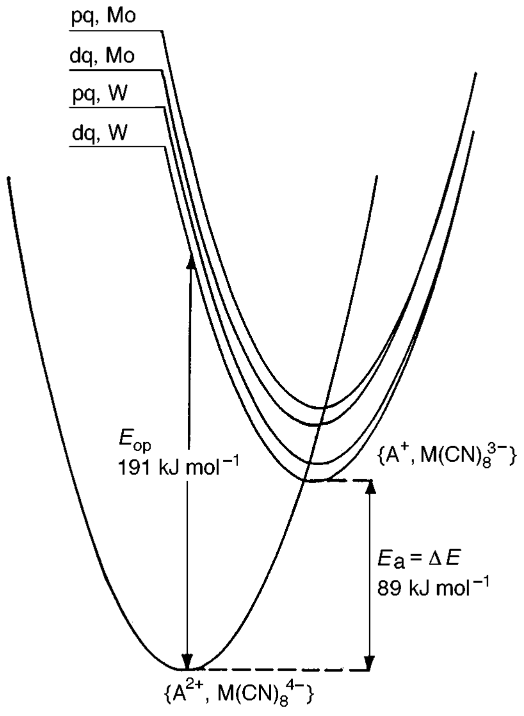


Fig. 3 Potential-energy diagram for electron transfer within the $\{A^{2+}, M(CN)_8^{4-}\}$ ion pair

Solid-state properties

To get insight into the process of electron transfer in the solid state we have isolated the compounds of formula $[A]_2[M(CN)_8]\cdot nH_2O$. The paraquat salts crystallize in the form of reddish brown **1** or purple **2** needles. When taken out of their original solutions both compounds immediately lose water of crystallization and the crystal collapse. The resulting emerald-green **1** and grass-green **2** powders were shown to be anhydrous. The diquat salts crystallize as stable pentahydrates $[dq]_2[M(CN)_8]\cdot 5H_2O$ in the form of purple **3** or green **4** needles (the characterization and structures of the last salts will be reported separately[11]). All four compounds are soluble in water and insoluble in common organic solvents. They are photosensitive as solids and in solution due to the photosubstitutional reactivity of octacyanometalates(IV), but in diffuse light they remain unaltered for a long period.

The reflectance spectra (Fig. 4) show that in solid state the IPCT bands become stronger than in solution [by comparison with $M(CN)_8^{4-}$ d–d transitions] and shift to longer wavelengths: 890 **1**, 1012 **2**, 592 **3** and 710 **4**.[11] This bathochromic shift, observed also for other bipyridinium octacyano-molybdates and -tungstates,[3,4] can be related to the close interaction of ions.

The ESR spectra of the salts show weak bands at $g_{av} = 1.994$ **1** and 1.972 **2**, **4** characteristic for d^1 centres of M^V but without the fine structure. The quantitative analysis of these bands

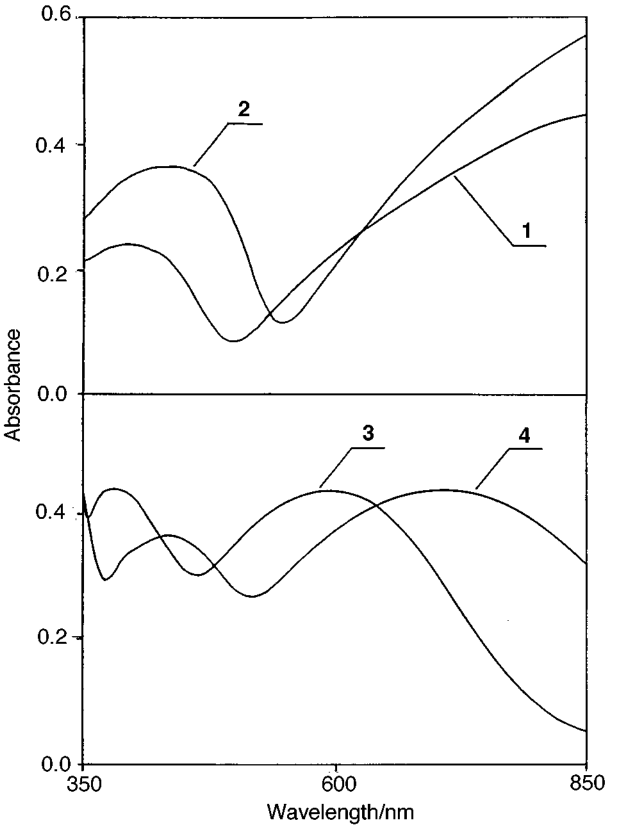


Fig. 4 Diffuse reflectance spectra of $[pq]_2[Mo(CN)_8]$ **1**, $[pq]_2[W(CN)_8]$ **2**, $[dq]_2[Mo(CN)_8]\cdot 5H_2O$ **3** and $[dq]_2[W(CN)_8]\cdot 5H_2O$ **4**

indicates the presence of 0.01 **1**, 1.50 **2** and 0.67% **4** of M^V in the salts (compound **3** was diamagnetic). The phenomenon of partial electron delocalization in IPCT complexes, observed also for the other bipyridinium octacyanometalates,[2–4] still requires more study for a full explanation.

The analysis of the $C\equiv N$ stretching region in the IR spectra and its comparison with the spectra of octacyanometalates of known structures[3,4,18] indicates that the symmetry of $M(CN)_8{}^{4-}$ in **1** and **2** is approximately antiprismatic (D_{4d}), unlike the almost dodecahedral (D_{2d}) anion in **3** and **4**.[11] The bands of cation origin, dominating the spectra of **1** and **2**, slightly change their position and intensity in comparison to those of $[pq]Cl_2\cdot H_2O$ (1353s, 1440w, 1507s, and 1643vs cm^{-1}). This shift can be attributed to hydrogen bonding between cyanide nitrogens and pyridine carbons, which was observed in the structures of **3** and **4**.[11]

Conclusion

The $\{A^{2+}, M(CN)_8{}^{4-}\}$ ion pairs exhibit optical charge transfer as indicated by the presence of IPCT absorption bands in the visible region. The thermodynamic parameters of the process calculated on the basis of spectral and electrochemical data suggest very fast back electron transfer. Although according to the results presented here the possibility of photoredox reaction is low, the systems studied provide valuable information for further studies on charge-transfer ion pairs based on bipyridinium cations and mixed-ligand cyano complexes of molybdenum(IV) and tungsten(IV).

Acknowledgements

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