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Photoreactivity of octacyanotungstate(V) ion in non-aqueous solvents

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Abstract

The CTTM photolysis of $(TBA)_3W(CN)_8$ has been studied in MeOH, MeCN, DMF and Me_2SO. The quantum yields for the photochemical decomposition of $W(CN)_8^{3-}$ are 0.50 ∓ 0.02, 0.46 ∓ 0.01, 0.42 ∓ 0.02 and 0.29 ∓ 0.03 in MeOH, MeCN, DMF and Me_2SO, respectively. The detection of products has proved that photolysis induces a cyano ligand photolabilization in high quantum yield (Φ_{CN^-} 0.33 in Me_2SO) concomitant with photoproduction of W(VI) species. The process has been associated with the efficient population of LF excited state via internal conversion from CTTM excited state, leading to photolabilization and followed by inner-sphere redox process between generated reactive $W(CN)_7^{2-}$ and parent $W(CN)_8^{3-}$ according to $W(CN)_7^{2-} + W(CN)_8^{3-} \rightarrow (NC)_7W^{V}\text{–}NC\text{–}W^{V}(CN)_7^{5-} \rightarrow (NC)_7W^{VI}\text{–}NC\text{–}W^{IV}(CN)_7^{5-} \rightarrow W(CN)_7^{-} + W(CN)_8^{4-}$, affording $W^{VI}(CN)_7^{-}$ as the dominant photoproduct.

Introduction

It has been proved that the octacyanotungstate(V) ion possesses rather complex photochemistry, associated with its lowest energy charge-transfer-to-metal CTTM band ($1^2E_1 \leftarrow {}^2A_1$ excitation). The photolysis in aqueous solution of $W(CN)_8^{3-}$ proceeds through a intermolecular photoredox process [1–4] with a quantum yield of 0.81 over a wide pH range [2, 3]

$$W(CN)_8^{3-} + 2H_2O \xrightarrow[CTTM]{h\nu} W(CN)_8^{4-} + \dot{O}H + H_3O^+ \qquad (1)$$

It has been found that photoreduction of the $W(CN)_8^{3-}$ ion in hydroxylic solvents proceeds through a long lived intermediate ($\tau_{293K} = 5.34$ ms in H_2O), assigned to a radical complex, i.e. $W^{IV}(CN)_7\dot{C}N^{3-}$ [5]. A minor photosubstitution pathway, proceeding through the highly reactive coordinatively unsaturated species $W(CN)_7^{2-}$

$$W(CN)_8^{3-} \xrightarrow[CTTM]{h\nu} W(CN)_7^{2-} + CN^- \qquad (2)$$

which becomes solvated rapidly

$$W(CN)_7^{2-} + \text{solvent} \longrightarrow W(CN)_7\text{solv}^{2-} \qquad (3)$$

has been reported recently not only in aqueous and non-aqueous solvents but also in the glassy state [6] and poly(vinyl alcohol) film [7]. Under high light intensities photolysis in water and water–methanol leads to new photoproducts, based on W(VI), consisting of pentagonal-bipyramidal $W(CN)_6O^{2-}$ and $W(CN)_5O(OMe)^{2-}$ ions, respectively [8, 9]. The formation of these photooxidation products has been viewed as proceeding via a two-quantum process, involving, as a light absorbing intermediate, reactive radical complex $W(CN)_7\dot{C}N^{3-}$, leading to oxidation of the tungsten centre, concomitant with a ligand field photosubstitution by the solvent

$$\begin{tikzcd}
W(CN)_7\dot{C}N^{3-} + W(CN)_8^{3-} \arrow[r] & W(CN)_7\dot{C}N^{2-} + W(CN)_8^{4-} \arrow[d, "+H_2O"] \\
& W(CN)_6O^{2-} + 2HCN
\end{tikzcd} \qquad (4)$$

In order to gain further insight into the intriguing charge-transfer photochemistry of the octacyanotungstate(V) ion, the photolysis of $(TBA)_3W(CN)_8$ (TBA = n-tetrabutylammonium (+1) cation), which has significant solubility in polar organic solvents, in MeOH, MeCN, DMF and Me_2SO has been examined. The present study provides the evidence that the solvent is of primary importance as the factor influencing the photochemical properties of the $W(CN)_8^{3-}$ ion and it also reveals the W(VI) cyano complexes to be characteristic final products not only in hydroxylic solvents but also in aprotic media.

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Experimental

Materials

The syntheses were carried out in red light. The preparation of $K_3W(CN)_8 \cdot 1.5H_2O$ has been described previously [2]. The salt $(TBA)_3W(CN)_8$ was prepared by mixing saturated solutions of (TBA)Cl (Fluka) in H_2O–MeOH (1:1 vol./vol.) and $K_3W(CN)_8$ in H_2O, with the latter in stoichiometric excess, filtering off precipitated $(TBA)_3W(CN)_8$ and, after washing with H_2O and drying, recrystallizing from MeOH. The compound purity was checked by means of the UV–Vis absorption spectrum. The *p*-benzoquinone (POCh) was purified by sublimation. All other chemicals were commercial products of reagent grade and used without further purification. Organic solvents, MeOH (POCh), MeCN (Romil), DMF (POCh) and Me_2SO (Aldrich), were of spectroscopic grade and dried according to literature procedures [10].

Apparatus and procedures

UV–Vis spectra were recorded with a M-40 (C. Zeiss, Jena) spectrophotometer which, equipped with a fluorimeter unit, was also used for the CN^- ion analyses. ESR spectra were recorded with a ESR 220 X-band spectrometer (GDR) at ambient temperature. Conventional flash photolysis was performed by means of an apparatus described elsewhere [11]. The xenon photoflash lamp was typically fired with 400 J energy (pulse width 20 μs). The radiation from the spectroflash between 37 000 and 13 000 cm^{-1} was recorded. The flash photolysis experiments were carried out in sample solutions of 2.5×10^{-5} mol dm^{-3} of $(TBA)_3W(CN)_8$ in an appropriate solvent, deaerated by Ar gas purging over 1 h. Steady-state photolyses were performed with the focused output of a XBO 150 lamp equipped with 10 cm path length quartz cell filled with H_2O for cutting off infrared radiation. The photoreduction of $W(CN)_8^{3-}$ in aqueous acidic solution ($\Phi = 0.81$) [3] was used as the actinometer. The experiments were performed with the unfiltered lamp output of 2.13×10^{16} quanta s^{-1} and filtered to isolate the 365 nm line (UV SIF 365 nm interference filter, C. Zeiss, Jena) of 1.55×10^{15} quanta s^{-1}. The concentration of $(TBA)_3W(CN)_8$ complex in an appropriate solvent varied within the range 5×10^{-4} to 1×10^{-2} mol dm^{-3}. The diluted solutions ($c < 2 \times 10^{-3}$ mol dm^{-3}) were partially transmitting, and the absorbed energy was evaluated according to ref 12. The experiments were carried out in aerated and deaerated (Ar purged) solutions. All solutions were protected from light by means of Al foil covered containers. All measurements were performed at ambient temperature. Photoreleased CN^- ion was determined spectrofluorometrically by the *p*-benzoquinone method [13], as the resulting fluorescent 2,3-dicyanohydroquinone at excitation and emission wavelengths of 400 and 480 nm, respectively. No fluorescence from unphotolyzed $(TBA)_3W(CN)_8$ in the presence of *p*-benzoquinone was observed.

Thin-layer chromatography (TLC) was performed by means of aluminium sheets coated with 0.2 mm thick silica gel 60 (Merck), with MeCN as eluent.

Results and discussion

The electronic spectrum of the $W(CN)_8^{3-}$ ion exhibits three CTTM bands with the lowest energy CTTM band covering two LF transitions [5]. The assignment of the electronic spectrum of $W(CN)_8^{3-}$, absorption maxima and molar extinction coefficients of $K_3W(CN)_8$ in various solvents have been reported previously [5]. Table 1 summarizes the absorption features of the lowest energy CTTM band of $(TBA)_3W(CN)_8$ in various solvents. The remarkably small sensitivity of the CTTM band of $W(CN)_8^{3-}$ to the nature of solvent can be accounted for in terms of only small perturbation in the electron density distribution within the complex, produced by donor–acceptor interactions between cyano ligands and solvent molecules [14], due to highly symmetrical electron density distribution in the homoleptic $W(CN)_8^{3-}$ ion (D_{4d} symmetry). This accords with the interpretation of the increasing solvent-shift effect along the series of Ru(II) complexes, on going from homoleptic $Ru(bpy)_3^{2+}$ to $Ru(bpy)_2(CN)_2$ and $Ru(bpy)(CN)_4^{2-}$ [15] and is also consistent with the model of solvatochromic effect proposed for mixed cyano–bipyridyl complexes of W(IV) [16].

Flash photolysis

Flash photolysis of MeOH solutions of $(TBA)_3W(CN)_8$ generates strongly absorbing species centred on λ_{max} 400 nm, being in full agreement with the results obtained by 249-nm laser flash pho-

TABLE 1. UV–Vis spectral data for $(TBA)_3W(CN)_8$ in different solvents

Solvent	$10^{-3} \times \tilde{\nu}$ (cm^{-1})	$10^{-3} \times \epsilon$ (dm^3 mol^{-1} cm^{-1})
py	27.56	1.818
DMF	27.56	1.989
Me_2SO	27.60	2.162
MeCN	27.80	1.935
MeOH	27.88	1.995
H_2O	27.96	1.778

tolysis, and assigned to a radical complex $W^{IV}(CN)_7\dot{C}N^{3-}$ ($\tau_{293K} = 90.9$ ms in MeOH) as the intermediate in the intermolecular photoredox pathway (eqn. (1)). Flash photolysis measurements of MeCN, DMF and Me_2SO solutions of $(TBA)_3W(CN)_8$ failed to give evidence of any transient species in a time longer than 20 μs.

Steady-state photolysis

Figure 1 shows the spectral changes induced by CTTM irradiation of diluted ($c = 1.1 \times 10^{-3}$ mol dm^{-3}) $W(CN)_8{}^{3-}$ solutions in MeOH. The principal feature of the spectral changes is a decrease in the $W(CN)_8{}^{3-}$ band with an increase in a weak visible absorption without any isosbestic points. The analogous behaviour is observed when the solutions are Ar purged (Fig. 1, inset). Figure 2 shows the spectral changes induced by CTTM irradiation of more concentrated ($c = 5 \times 10^{-3}$ mol dm^{-3}) $W(CN)_8{}^{3-}$ solutions in MeOH. Under these conditions, a decrease of the 27 880 cm^{-1} band concomitant with the increase of broad absorbance centred at 25 800 cm^{-1} is observed during the irradiation. Photolysis of $(TBA)_3W(CN)_8$ in MeCN ($c > 5 \times 10^{-4}$ mol dm^{-3}) (Fig. 3) results in the production of a new absorbance centred on 23 200 and 18 800 cm^{-1}, more efficient in the absence of oxygen (Fig. 3, inset). Figure 4 shows the spectral changes induced by the irradiation of $(TBA)_3W(CN)_8$ in DMF. A decrease of the 27 560 cm^{-1} band and the increase of the absorbance centred on 26 520, 23 000 and 18 000 cm^{-1} are observed during the irradiation. The presence of oxygen inhibits this process (Fig. 4, inset). Figure 5 shows the spectral changes induced by the irradiation of $(TBA)_3W(CN)_8$ in Me_2SO. A decrease of the 27 600 cm^{-1} band concomitant with the increase of the broad absorbance centred on 23 280 and 18 000 cm^{-1} is observed during the irradiation. Production of a new absorbance is inhibited by the presence of oxygen (Fig. 5, inset). The analogous photolyses carried out with the 365nm irradiation line (in MeCN and DMF) show that the spectra of irradiated $W(CN)_8{}^{3-}$ feature a decrease in the $W(CN)_8{}^{3-}$ band with an increase

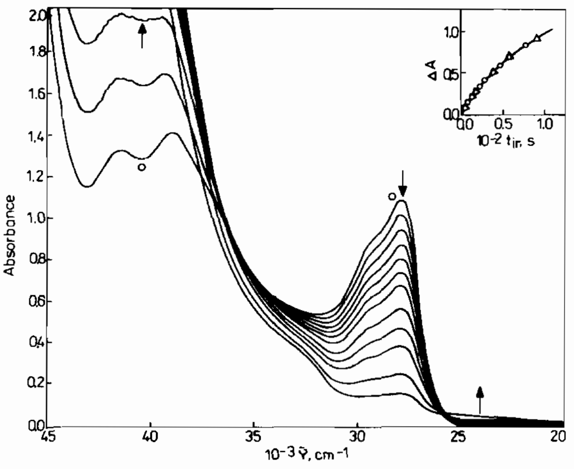

Fig. 1. Spectral changes induced by the continuous irradiation of Ar purged solution of 1.1×10^{-3} mol dm^{-3} $(TBA)_3W(CN)_8$ in MeOH. Optical path = 0.5 cm. Spectrum of unirradiated solution (O); the other spectra were obtained after 5, 10, 15, 20, 25, 30, 40, 50, 60, 80 and 100 s of irradiation, respectively, with the arrows indicating the direction of the changes. Inset: $\Delta A = A_0 - A_i$ at 27 870 cm^{-1} as a function of time of irradiation for Ar purged (O) and aerated solutions (△).

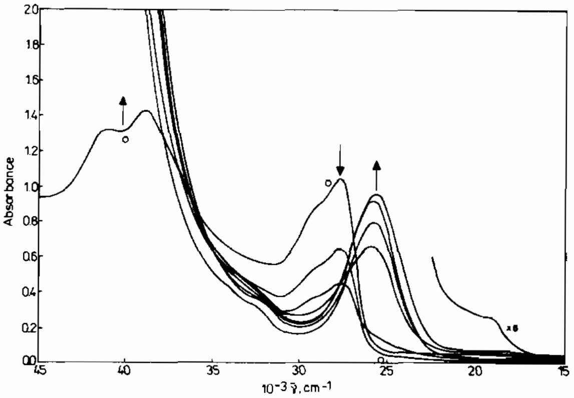

Fig. 2. Spectral changes induced by the continuous irradiation of aerated solution of 5×10^{-3} mol dm^{-3} $(TBA)_3W(CN)_8$ in MeOH. Optical path = 0.5 and 0.1 cm for irradiation and recording, respectively. Spectrum of unirradiated solution (O); the other spectra were obtained after 30, 60, 90, 120, 180 and 240 s of irradiation, respectively, with the arrows indicating the direction of the changes.

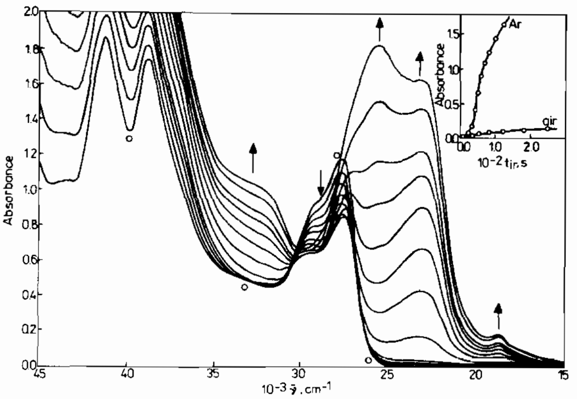

Fig. 3. Spectral changes induced by the continuous irradiation of Ar purged solution of 1.2×10^{-3} mol dm^{-3} $(TBA)_3W(CN)_8$ in MeCN. Optical path = 0.5 cm. Spectrum of unirradiated solution (O); the other spectra were obtained after 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 100 and 120 s of irradiation, respectively, with the arrows indicating the direction of the changes. Inset: absorbance at 23 200 cm^{-1} as a function of time of irradiation for Ar purged and aerated solutions.

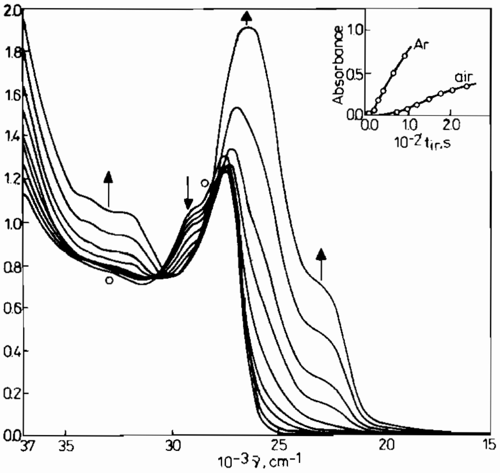

Fig. 4. Spectral changes induced by the continuous irradiation of Ar purged solution of 1.3×10^{-3} mol dm^{-3} $(TBA)_3W(CN)_8$ in DMF. Optical path = 0.5 cm. Spectrum of unirradiated solution (O); the other spectra were obtained after 5, 10, 15, 20, 30, 40, 60 and 90 s of irradiation, respectively, with the arrows indicating the direction of the changes. Inset: absorbance at 23 000 cm^{-1} as a function of time of irradiation for Ar purged and aerated solutions.

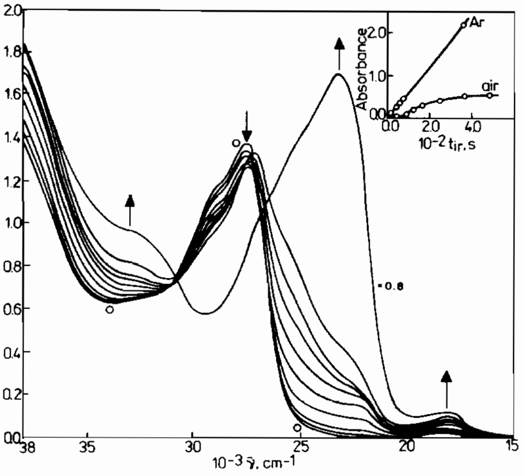

Fig. 5. Spectral changes induced by the continuous irradiation of Ar purged solution of 1.3×10^{-3} mol dm^{-3} $(TBA)_3W(CN)_8$ in Me_2SO. Optical path = 0.5 cm. Spectrum of unirradiated solution (O); the other spectra were obtained after 5, 10, 20, 30, 40, 50, 60, 80 and 330 s of irradiation, respectively, with the arrows indicating the direction of the changes. Inset: absorbance at 23 280 cm^{-1} as a function of time of irradiation for Ar purged and aerated solutions.

in a weak visible absorption. Exhaustive photolyses in all solvents studied result in complete bleaching of all observed absorption bands.

The following common features of the spectral changes induced by the CTTM irradiation of $W(CN)_8^{3-}$ in the solvents employed have been established: (i) decrease in the CTTM band of $W(CN)_8^{3-}$, which has been attributed to the disappearance of $W(CN)_8^{3-}$ and formation of $W(CN)_8^{4-}$ (the characteristic features of the $W(CN)_8^{4-}$ ion are the maxima at 39 900 (ϵ 2.460×10^4), 27 000 (ϵ 240.0) and a plateau at 23 200 cm^{-1} (ϵ 118.6) in $MeOH/H_2O$ (24:1 vol./vol.); (ii) increase of the intensive absorbance in the visible part of the spectra with the features indicating the presence of a few components; (iii) inhibiting role of oxygen on the photochemical pathway, suggesting that the new photoproducts are not formed in secondary process by oxidation of primary photoproducts with O_2; (iv) sensitivity to the concentration of the parent $W(CN)_8^{3-}$ as illustrated in the case of hydroxylic MeOH solvent. The quantum yield values determined in terms of the disappearance of $W(CN)_8^{3-}$ have been estimated, assuming the negligible contribution of new photoproducts at the maximum of the CTTM band of $W(CN)_8^{3-}$ (*vide infra*) for small photochemical conversion ($<10\%$). The quantum yield values have been calculated assuming $\Delta\epsilon = 1.781\times10^3$, 1.712×10^3, 1.764×10^3 and 1.789×10^3 dm^3 mol^{-1} cm^{-1} in MeOH, MeCN, DMF and Me_2SO, respectively, on the assumption that only $W(CN)_8^{4-}$ contributes to the absorbance values at the CTTM band's maximum of $W(CN)_8^{3-}$*. The Φ values calculated assuming such estimated $\Delta\epsilon$ values slightly decrease with increasing time of irradiation (the results can be accounted for in terms of thermal back reaction and/or increasing contribution from other photoproducts (inner filter effect)). The initial quantum yield values Φ^0 obtained from the extrapolation of the data to zero time of irradiation approach the values of 0.50 ∓ 0.02, 0.46 ∓ 0.01, 0.42 ∓ 0.02 and 0.29 ∓ 0.03 in aerated MeOH, MeCN, DMF and Me_2SO solutions, respectively. In the absence of oxygen, the Φ^0 values of 0.51, 0.53, 0.41 and 0.21 are obtained in MeOH, MeCN, DMF and Me_2SO, respectively. While the quantum yield Φ^0 in MeOH is practically unaffected by the presence of oxygen, the quantum yield values in deaerated MeCN, DMF and Me_2SO differ slightly from those obtained in aerated solutions. The plausible explanation of this effect is that in deaerated solutions the irradiation gave rise to faster and more efficient formation of the new absorption bands, contributing to the absorbance at the CTTM maximum of $W(CN)_8^{3-}$. The presence of oxygen inhibits this

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*Molar extinction coefficients of $W(CN)_8^{4-}$ in appropriate organic solvent have been estimated from the spectra of $K_4W(CN)_8$ in solvent–H_2O (24:1 vol./vol.) media; in DMF and Me_2SO the molar extinction coefficients were obtained from kinetic data due to rapid oxidation of $W(CN)_8^{4-}$ to $W(CN)_8^{3-}$ in aerated solutions.

process and results in the initial quantum yield values more representative of the disappearance of $W(CN)_8{}^{3-}$. The quantum yield values are found to be solvent-dependent. The Φ^0 of the disappearance of $W(CN)_8{}^{3-}$ decreases in the order MeOH > MeCN > DMF > Me_2SO in both, aerated and deaerated solutions. The 365 nm photolyses carried out in aerated MeCN and DMF solutions cause the decrease of the CTTM band of the parent $W(CN)_8{}^{3-}$ ion with an initial quantum yield Φ^0 of 0.53 and 0.49, respectively, not significantly different from those obtained in polychromatic light.

Spectral changes induced by CCTM excitation of $W(CN)_8{}^{3-}$ are accompanied by photochemical release of free CN^- ions. Figure 6 shows the increase of concentration of photolabilized CN^- ions with increasing time of irradiation in photolyzed $(TBA)_3W(CN)_8$ in Me_2SO. The initial quantum yield value $\Phi^0_{CN^-}$, obtained from the extrapolation of the plot of $\Phi^{-1}_{CN^-}$ versus t_{ir} to zero time of irradiation (up to 15% conversion) approaches the value of 0.33 in aerated Me_2SO. The results obtained with this system can be accounted for in terms of a competition between photolabilization of CN^- ions and the back recombination of the cyanotungstate moiety with CN^- ion and/or secondary reaction of CN^- ions.

Irradiation of $W(CN)_8{}^{3-}$ in all solvents studied induces a gradual decrease of the original ESR absorption of $W(CN)_8{}^{3-}$ at g_{av} = 1.9686, 1.9689, 1.9696 and 1.9686 in MeOH, MeCN, DMF and Me_2SO, respectively*, indicating the formation of diamagnetic photoproducts in the time scale of the experiments.

In spite of the complexity of the irradiated $(TBA)_3W(CN)_8$ in organic solvent systems the separation of a post-irradiated reaction mixture has been performed by thin layer chromatography (TLC). Apart from unreacted $(TBA)_3W(CN)_8$, three fractions are resolvable from irradiated 1×10^{-2} mol dm^{-3} $(TBA)_3W(CN)_8$ in MeCN: an orange one with the value of $R_f = 0.59$, yellow with $R_f = 0.51$ and violet with $R_f = 0.30$. The photoproducts mixture appears to consist largely of yellow species (species I), with minor contributions from orange species (species II) and violet one (species III). Figure 7 shows the visible absorption spectra of these three photoreaction products, characterized by the bands at 24 160 (species I), 20 960 (species II) and 18 800 (species III) cm^{-1}. All attempts to detect the species characterized by the absorption band centred at 26 000 cm^{-1}, have been unsuccessful. The spectral characteristics of the photoproducts from irradiated $(TBA)_3W(CN)_8$ in other solvents studied, obtained on TLC separation, are summarized in Table 2.

A clue to the nature of species I, II and III comes from the X-ray photoelectron spectroscopy (XPS) study. The systematic XPS study of cyano complexes of tungsten, which will be published elsewhere [17], reveals that (i) the W 4f spectra of species I and II consists of peaks due to W(VI) only, while the W 4f spectrum of species III shows peaks corresponding to W(VI) and W(IV); (ii) the N 1s spectra of species I, II and III can be attributed to the

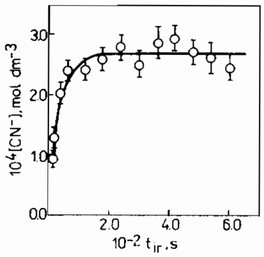

Fig. 6. Values of the concentration of photoreleased CN^- ions as a function of time of irradiation in aerated 1.28×10^{-3} mol dm^{-3} $(TBA)_3W(CN)_8$ in Me_2SO.

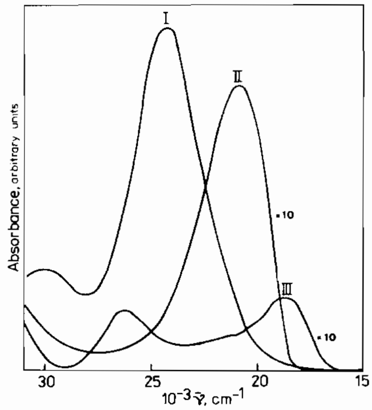

Fig. 7. The visible absorption spectra of three photoproducts obtained by TLC separation of irradiated 1×10^{-2} mol dm^{-3} $(TBA)_3W(CN)_8$ in MeCN.

TABLE 2. Visible absorption spectra of the photoproducts of $(TBA)_3W(CN)_8$ in non-aqueous solvents[a]

Photoproduct	$10^{-3}\times\bar{\nu}_{max}$ (cm^{-1})		
	MeOH	MeCN	DMF
Species I	24.04	24.16	24.08
Species II	21.12	20.96	22.00
Species III	17.64	18.80	18.00

[a] Photolysis of 1×10^{-2} mol dm^{-3} $(TBA)_3W(CN)_8$, t_{ir} = 10 min, optical path = 0.5 cm, aerated solutions.

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*The small differences between g_{av} values obtained in this work and those reported previously [6] are probably due to different countercation used.

structurally distinguishable types of nitrogen atoms, i.e. to the tetrabutylammonium cation and cyano ligands nitrogen atoms. The W 4f and N 1s spectra are consistent with the assignment of species I to the mononuclear $W^{VI}(CN)_7^-$ complex. Species II is attributed to a dinuclear W(VI), possibly cyano-bridged, complex of tentative formula $W_2(CN)_{13}^-$ ([6, 6] notation). The W 4f and N 1s spectra of species III suggest a trinuclear [6, 4, 6], possibly cyano-bridged, complex of tentative formula $W_3(CN)_{22}^{6-}$.

The intense absorption bands in the visible region of the electronic spectra of $W(CN)_7^-$ and $(CN)_6W^{VI}$–NC–$W^{VI}(CN)_6^-$ must be related to the charge-transfer transitions (since there are no d electrons in the $5d^0$ W(VI) system, these bands are not attainable from analysis of d–d transitions) from strongly donating coordinated cyano ligands [18–21] to the tungsten(VI) centre (LMCT transitions). Further support of this assignment comes from the interpretation of the electronic spectrum of the homoleptic $W^{VI}(NMe_2)_6$ complex [22]. The band at *c.* 18 800 cm^{-1} (in MeCN) of the trinuclear [6, 4, 6] species, which gives the violet colour, can be assigned to the MMCT transition from the reducing W(IV) centre to one of the oxidizing W(VI) centres, i.e., $[6, 4, 6] \xrightarrow{\text{MMCT}} [6, 5, 5]$. This assignment requires the weak metal–metal electronic coupling provided by the cyano bridge.

The results presented above show that CTTM excitation of the $W(CN)_8^{3-}$ ion in non-aqueous solvents leads to the efficient CN^- release and photoproduction of tungsten(VI) species. Although the photoproducts are the same in each of the solvents studied, it has been proved that the formation of the radical complex $W(CN)_7\dot{C}N^{3-}$ takes place only in hydroxylic MeOH solvent. Therefore, the photoproduction of W(VI) species cannot be related to the two-quantum process involving $W(CN)_7\dot{C}N^{3-}$ as a light-absorbing intermediate, proposed for the high-intensity photolysis in aqueous solution (eqn. (4)). In order to maintain the $W(CN)_8^{3-}$ photochemistry model, the formation of W(VI) species can be explained if the photoreactivity is associated with the LF excited state, which, populates via internal conversion from the CTTM excited state [5, 23], generates $W(CN)_7^{2-}$ (eqn. (2)) [6, 7]. In the case of hydroxylic MeOH solvent, the labilization of the cyano ligand must compete with the intermolecular photoredox pathway (eqn. (1)). On the other hand, primary photooxidation of the solvent is not expected to be favourable from the redox point of view in other aprotic solvents studied, supported by the drastic shift in $E_{1/2}$ for the $W(CN)_8^{4-}/W(CN)_8^{3-}$ couple on going from 0.51 (H_2O) and 0.32 (MeOH) to 0.26 (MeCN) and −0.06 V (Me_2SO) (versus NHE) [24]. One possible explanation for the photoproduction of $W(CN)_7^-$ is that the primary photodissociation step, generating reactive, coordinatively unsaturated $W(CN)_7^{2-}$ species, is followed by the redox reaction

$$W(CN)_7^{2-} + W(CN)_8^{3-} \longrightarrow W(CN)_7^- + W(CN)_8^{4-} \qquad (5)$$

leading to the formation of $W(CN)_7^-$ and $W(CN)_8^{4-}$, as identified. The failure to detect the species, exhibiting the characteristic intense absorbance centred on *c.* 26 000 cm^{-1}, can be explained if the overall redox reaction (5) is considered as the inner-sphere redox process according to

$$\begin{aligned} &W(CN)_7^{2-} + W(CN)_8^{3-} \longrightarrow \\ &\quad (CN)_7W^{V}\text{–NC–}W^{V}(CN)_7^{5-} \longrightarrow \\ &\quad (CN)_7W^{VI}\text{–NC–}W^{IV}(CN)_7^{5-} \longrightarrow \\ &\quad W(CN)_7^- + W(CN)_8^{4-} \end{aligned} \qquad (6)$$

and the binuclear redox isomer [6, 4], sufficiently long-lived to be observed in irradiated solutions and responsible for the absorbance at 26 000 cm^{-1}, dissociates into the mononuclear complexes $W(CN)_7^-$ and $W(CN)_8^{4-}$. The binuclear successor complex [6, 4] can be stabilized by the formation of trinuclear [6, 4, 6] species

$$(CN)_7W^{VI}\text{–NC–}W^{IV}(CN)_7^{5-} + W(CN)_7^- \longrightarrow (CN)_7W^{VI}\text{–NC–}W^{IV}(CN)_6\text{–CN–}W^{VI}(CN)_7^{6-} \qquad (7)$$

as identified. The presence of $W_2(CN)_{13}^-$ suggests the formation of binuclear [6, 6] species according to

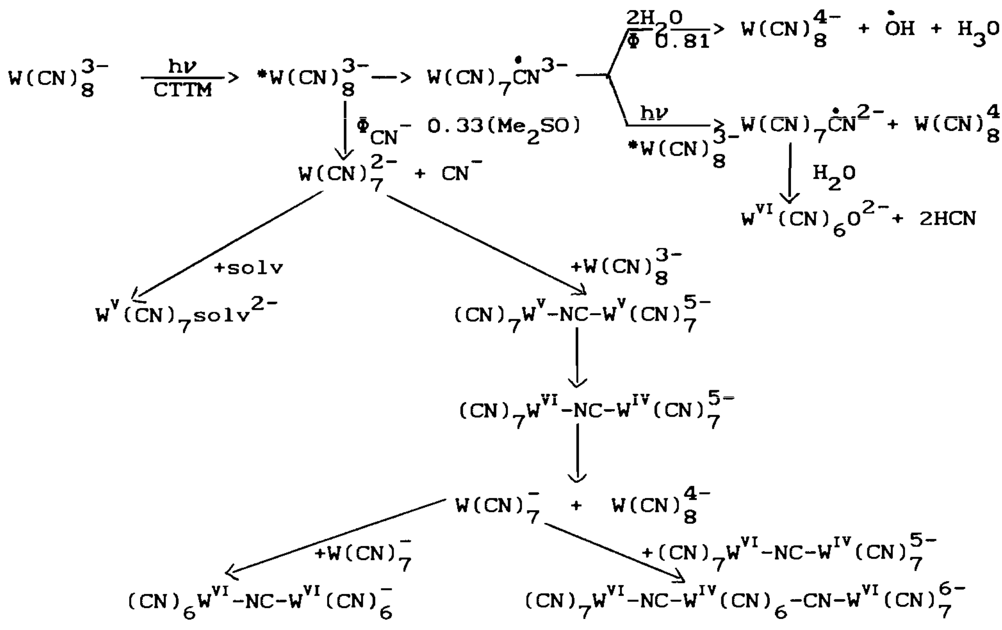
$$2W(CN)_7^- \longrightarrow (CN)_6W^{VI}\text{–CN–}W^{VI}(CN)_6^- + CN^- \qquad (8)$$

These results clearly establish the ability of octacyanotungstate(V) to photoproduce W(VI) species in high efficiency in non-aqueous solvents under CTTM excitation.

Conclusions

On the basis of the results presented here and those discussed previously [1–9], the general scheme of photoreactivity of the $W(CN)_8^{3-}$ ion is as presented in Scheme 1.

The photoredox reactivity has been associated with the efficient population of the CTTM excited state, generating the radical complex $W(CN)_7\dot{C}N^{3-}$, which, via oxidation of hydroxylic solvent, produces $W(CN)_8^{4-}$. Highly endoergonic photoproduction of



Scheme 1.

$W^{VI}(CN)_6O^{2-}$ has been attributed to a two-quantum process involving $W(CN)_7\dot{C}N^{3-}$ as a light-absorbing intermediate. A mechanism by which excitation can induce photoproduction of W(VI) species in non-aqueous solvents consists in the population of LF excited state via internal conversion from CTTM excited state, leading to the formation of highly reactive, unsaturated $W(CN)_7^{2-}$ species, which via an inner-sphere redox process with the parent $W(CN)_8^{3-}$ produce the dominant seven-coordinate $W^{VI}(CN)_7^-$ ion and $W(CN)_8^{4-}$. The photoproduction of dinuclear $(CN)_6W^{VI}\text{-CN-}W^{VI}(CN)_6^-$ and trinuclear $(CN)_7W^{VI}\text{-NC-}W^{IV}(CN)_6\text{-CN-}W^{VI}(CN)_7^{6-}$ complexes has been attributed to dimerization of $W(CN)_7^-$ and reaction of binuclear $(CN)_7W^{VI}\text{-NC-}W^{IV}(CN)_7^{5-}$ with $W^{VI}(CN)_7^-$, respectively.

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