Electron Spin Resonance Studies of the Solution Photochemistry of Octacyanotungstate(V) Ions at 77 and 293 K [*]

Terence J. Kemp and Mark A. Shand
Department of Chemistry, University of Warwick, Coventry CV4 7AL
Detlef Rehorek
Sektion Chemie, Karl-Marx-Universität, Talstrasse 35, Leipzig 7010, German Democratic Republic

---

While the photolysis of aqueous solutions of $[W^{V}(CN)_8]^{3-}$ in its charge-transfer-to-metal band proceeds largely (90%) through a photoredox process, *ca.* 10% proceeds through the transient $[W^{V}(CN)_7]^{2-}$ which either becomes solvated rapidly to give $[W^{V}(CN)_7(H_2O)]^{2-}$ or, in the presence of high concentrations of X^- ions (X = Cl, Br, N_3, or SCN) or O_2, reacts to give $[W^{V}(CN)_7X]^{3-}$ or $[W^{V}(CN)_7(O_2)]^{2-}$ respectively, characterised by their *g*-tensors. $[W^{V}(CN)_7]^{2-}$ is detected directly only on photolysis at 77 K with $g_{\perp} = 1.918$, $g_{\parallel} = 2.010$, although it can be spin-trapped, while $[W^{V}(CN)_7(H_2O)]^{2-}$ is detected after warming photolysed glasses to 293 K followed by recooling to 77 K (at 77 K $g_{\perp} = 1.918$, $g_{\parallel} = 2.020$, $g_{av.} = 1.952$; at 293 K $g_{iso.} = 1.947$). $[W^{V}(CN)_7(H_2O)]^{2-}$ reacts with $[W(CN)_8]^{4-}$ to give $[(CN)_7W^{V}(CN)W^{IV}(CN)_7]^{6-}$ with $g_{iso.} = 1.944$, $g_{\perp} = 1.883$, and $\lambda_{max.} = 1\,350$ nm, and with $[Fe(CN)_6]^{3-}$ to give $[(CN)_5Fe^{II}(CN)W^{V}(CN)_7]^{6-}$ with $g_{iso.} = 1.9398$. In confirmation, oxidation of $[W^{IV}(CN)_7(H_2O)]^{3-}$ by Ce^{IV} or H_2O_2 yields initially $[W^{V}(CN)_7(H_2O)]^{2-}$ which on standing is converted slowly to $[(CN)_7W^{V}(CN)W^{IV}(CN)_7]^{6-}$.

The accepted view until very recently has been that the main photochemical event following irradiation of $[W(CN)_8]^{3-}$ ions in aqueous solution in the charge-transfer-to-metal (c.t.t.m.) band at 355 nm is a redox process leading solely to $[W(CN)_8]^{4-}$ with a quantum yield of *ca.* 0.8 over a wide range of pH.[1] This has been viewed as an intermolecular process [equation (1)],[1–3]

$$[W(CN)_8]^{3-} + H_2O \xrightarrow[\text{c.t.t.m.}]{h\nu} [W(CN)_8]^{4-} + H^+ + {}^{\bullet}OH \quad (1)$$

although the analogous process for $[Mo(CN)_8]^{3-}$ has also been portrayed as intramolecular [equation (2)].[4,5] The involvement

$$[Mo(CN)_8]^{3-} \xrightarrow[\text{c.t.t.m.}]{h\nu} [Mo(CN)_7]^{3-} + {}^{\bullet}CN \quad (2)$$

of free radicals is confirmed by spin-trapping experiments; thus $^{\bullet}OH$ has been detected during photolysis of both octacyanometalates in aqueous solution,[6,7] $^{\bullet}OMe$[8,9] and $MeOCH{=}N^{\bullet}$ from $[Mo(CN)_8]^{3-}$ in methanol, and $^{\bullet}CN$ from $[Mo(CN)_8]^{3-}$ in CH_2Cl_2.[10] (The c.t.t.m. band at 355 nm in water is not shifted in MeOH or MeCN[11] but in CH_2Cl_2, pyridine, and dimethyl sulphoxide we find that it moves 4.5 nm to the red.)

New pathways are reported when anaerobic aqueous solutions of $[W(CN)_8]^{3-}$ are subjected to high-intensity irradiation (200- and 500-W lamps + WG-305 cut-off filter).[7] A new material having $\lambda_{max.}$ 535 nm appears, assigned to $[W^{IV}(CN)_7(O_2)]^{3-}$; this decays slowly to yield $[W(CN)_8]^{4-}$. Under alkaline conditions in the dark the species having $\lambda_{max.}$ 535 nm partially changes to a violet material, $\lambda_{max.}$ 560 nm, assigned to $[(CN)_7W(O_2)W(CN)_7]^{6-}$. Acidification of a solution of the latter leads to $[W(CN)_7(H_2O)]^{3-}$ ($\lambda_{max.}$ 520 nm)[12] plus the supposed $[W^{IV}(CN)_7(O_2)]^{3-}$.

Rather few e.s.r. studies concentrating on the metal centre have been carried out, but Sieklucka *et al.*[7] report that irradiation of $[W(CN)_8]^{3-}$ (0.01 mol dm^{-3}) in water–methanol (1:1) causes a gradual disappearance of the well known octacyanotungstate spectrum (variously reported with $g_{av.} = 1.972$[13] and 1.9706[14]) and the appearance of a new weak signal (*ca.* 5—10% original signal intensity) with $g_{av.} = 1.943$, assigned tentatively to $[W(CN)_7(H_2O)]^{2-}$.

The present paper describes both the room- and low-temperature photolysis of aqueous solutions of salts containing $[W(CN)_8]^{3-}$, both alone and in the presence of high concentrations of simple anions, of other metal cyanide complexes, and of O_2. Solutions in a variety of organic solvents have also been investigated. Many different types of product based on W^{V} are found and identified mainly through their e.s.r. spectra: all reactions are considered to involve a common initial intermediate, namely $[W(CN)_7]^{2-}$.

Experimental

Materials.—$K_3[W(CN)_8]{\cdot}1.5H_2O$ was prepared by oxidation of $K_4[W(CN)_8]{\cdot}2H_2O$[15] using aqueous acidic potassium permanganate.[3] The $[EPh_4]^+$ salts (E = P or As) were obtained by precipitation from an aqueous solution of the potassium salt on addition of $[EPh_4]Cl$ (Aldrich) and purified by recrystallisation from aqueous acetone. Nitrosodurene was prepared according to Smith and Taylor.[16] *N*-(Benzylidene)-t-butylamine *N*-oxide (bbao) and its 2-sulphonated derivative were prepared by condensation of benzaldehyde and 2-sulphonatobenzaldehyde, respectively, with hydroxy-t-butyl amine.[17] Solvents were of spectroscopic grade.

Equipment and Procedures.—E.s.r. spectra were recorded with a Bruker model ER 200 tt instrument as described before.[18] Irradiation was carried out with a Hanovia 100-W Xe/Hg point-source lamp equipped with either band-pass glass filters or Balzer metal interference filters. A quartz e.s.r. cell attached to an H-shaped mixing chamber was used, and solutions were deoxygenated by bubbling with argon or O_2-free nitrogen for at least 20 min prior to photolysis. The octacyanide salts used were 0.01 mol dm^{-3} and the spin-traps 0.05 mol dm^{-3}. Coupling constants and *g*-tensors are averaged values from at least three independent measurements and errors are given in footnotes to the Tables.

[†] *Non-S.I. unit employed:* G = 10^{-4} T.

Table 1. Tungsten(v) species detected during photolysis of $K_3[W(CN)_8]$ in anaerobic aqueous solution (0.01 mol dm^{-3}) at 293 K[a]

	Species (I)		Species (II)		Species (III)		Species (IV)		
Sample	*g*	*a*(W)	*g*	*a*(W)	*g*	*a*(W)	*g*	*a*(W)	Other species and comments
Buffered to pH 7	1.9705	55.6			1.9474	59.5			
30% $HClO_4$	1.9705	55.6			1.9488	54.0			Blue-violet colour develops
Oxygenated	1.9705				1.9470		1.9450		
+bbao	1.9705		1.9670		1.9477				Spin-adduct detected: $a(^{14}N)$ = 15.74, $a(^{1}H)$ = 2.91, assigned to $^{\bullet}OH$ adduct[b]
+NaN_3 (3.0 mol dm^{-3})	1.9705	55.6	1.9570	56.4	1.9466		1.9442		(II) dominant; deep red solution; $N_3^{\bullet}$ spin-trapped [$a_1(N)$ = 15.08, $a_2(N) = a(H)$ = 2.05]
+LiCl (9.0 mol dm^{-3})	1.9705		1.9596				1.9440		
+KCl (3.0 mol dm^{-3})	1.9705	55.6	1.9587				1.9443	57.1	
+KBr (3.0 mol dm^{-3})	1.9705	55.6	1.9798[c]				1.9440	57.2	
+KI (2.0 mol dm^{-3})	1.9705	55.6			1.9475	59.5			I_3^- formed on mixing, *g* = 1.9394
+KSCN	1.9705		1.9652 1.9524						
+KOCN (1.0 mol dm^{-3})	1.9705	55.6			1.9475				
+$NaNO_2$ (1.0 mol dm^{-3})	1.9705	55.6			1.9479	59.5			Also *g* = 2.0006, $a(^{14}N)$ = 13.5, due to $[W(CN)_7(NO)]^{3-}$
+$NaClO_4$ (3.0 mol dm^{-3})	1.9705	55.6			1.9466		1.9440	57.2	Line at *g* = 1.9657 (hyperfine?) disappears on terminating photolysis; $CO_2^{\bullet-}$ spin-trapped
+NaO_2CMe (3.0 mol dm^{-3})	1.9705	55.6			1.9483	59.5			
+$K_4[Fe(CN)_6]$					1.9475	61.9			Strong signal decays on termination of photolysis with $t_{\frac{1}{2}}$ = 29 s
+$K_4[Ru(CN)_6]$	1.9705				1.9474	61.9			Signal decays after photolysis
+$K_4[Os(CN)_6]$	1.9705				1.9466				Very weak signal

[a] *a* Values in G: *g* values ±0.0005, *a* values ±0.5 G. *a*(W) refers to ^{183}W. [b] *cf.* Literature data for $^{\bullet}OH$ adduct (E. G. Janzen, D. E. Nutter, jun., E. R. Davies, B. J. Blackburn, J. L. Poyer, and P. B. McCay, *Can. J. Chem.*, 1978, **56**, 2237. [c] $a(^{79,81}Br)$ = 11.9.

Results and Discussion

General.—Irradiation of $[W(CN)_8]^{3-}$ ions in aqueous solution using either an interference filter (364 nm) or a combination of filters affording a broad band of wavelengths (350—600 nm) excites the 355 nm c.t.t.m. band of the complex. Such excitation induces a gradual decrease of the e.s.r. absorption of $[W(CN)_8]^{3-}$ (due mainly to the formation of diamagnetic W^{IV}) and the formation of various paramagnetic photoproducts containing W^{V} to an extent corresponding to *ca.* 10% of the original W^{V} signal intensity. This overall pattern is preserved when irradiations are carried out at 77 K. The precise nature of the W^{V} photoproducts depends on the conditions of photolysis, particularly the presence of simple anions (see below). Our basis for discussion of the results set out below is that while *ca.* 90% of the chemical decay of the c.t.t.m. excited state of $[W(CN)_8]^{3-}$ proceeds *via* the redox pathway, equation (1), some 10% proceeds *via* equation (3). All our results can be explained in

$$[W(CN)_8]^{3-} \xrightarrow[\text{c.t.t.m.}]{h\nu} [W(CN)_7]^{2-} + CN^- \quad (3)$$

terms of the products of reaction of the highly reactive coordinatively unsaturated species $[W(CN)_7]^{2-}$.

E.S.R. Studies of Photolysis of Solutions of $[W(CN)_8]^{3-}$ *Ions at Room Temperature.*—Both for aqueous and non-aqueous media, the e.s.r. spectra of a wide variety of irradiated solutions can be discussed in terms of just four paramagnetic species, (I)—(IV). The results for aqueous solutions are summarised in Table 1. Featuring three of the species (Figure 1) is the spectrum of aqueous $K_3[W(CN)_8]$ photolysed (364 nm) in the presence of NaN_3 (3.0 mol dm^{-3}), which shows unreacted $[W(CN)_8]^{3-}$ at *g* = 1.9705 [species (I)], a major signal at *g* = 1.9570 with $a(^{183}W)$ = 56.4 G [species (II)], and a minor signal at *g* = 1.9466 [species (III)], this solution is deep red ($\lambda_{max.}$ 425 nm). A further minor species (IV) at $g_{av.}$ = 1.9442 was evident under some conditions, and in general for aqueous solutions the relative concentrations of species (II)—(IV) in other photolysate solutions are highly dependent on the nature of the anion present (Table 1), and the only other aqueous solutions producing sizeable quantities of species (II) are those containing high concentrations of Br^-, Cl^-, or SCN^- ions. Photolysis in the presence of $[M(CN)_6]^{4-}$ ions (M = Fe, Ru, or Os) led to species (III)-type spectra.

Results for non-aqueous media are summarised in Table 2; species (II) and (III) are found in MeOH or MeOH–water systems: the appearance of species (III) in other solvents can be prevented by rigorous drying procedures.

The photolysis of $[PPh_4]_3[W(CN)_8]$ in MeCN–benzene (5:1, v/v) in the presence of nitrosodurene yielded a spin-trap product with $a(^{14}N)$ = 9.59 G, which is assigned below.

E.S.R. Studies of Photolysis of $[W(CN)_8]^{3-}$ *Ions at* 77 K.—Photolysis in the c.t.t.m. band at 77 K led to a single W^{V} product despite wide variation in the character of the solvent (Table 3). When $[W(CN)_8]^{3-}$ was *ca.* one-third destroyed it was found that there was *ca.* 10% conversion into the form of an axially symmetric species [species (V)] with $g_{\perp}$ = 1.918—1.920 and $g_{\parallel}$ = 2.010—2.021 [Figure 2(*a*)] for a solution in CH_2Cl_2. After warming the sample briefly (but to a temperature well below the melting point), and recooling to 77 K, two new species [(VI) and (VII)] were formed. Species (VI) is completely anisotropic, but g_2 could be measured in only two cases, while for species (VII) only $g_{\perp}$ was resolved, *e.g.* in Figure 2(*b*) for the same solution as in Figure 2(*a*) after warming and refreezing. Freezing to 77 K of a solution of $[W(CN)_8]^{3-}$ in 3.0 mol dm^{-3} sodium azide *after* photolysis at 293 K [when the e.s.r. spectrum is dominated by species (II)] led to an axially symmetric species with $g_{\perp}$ and $g_{\parallel}$ suggestive of species (V), Figure 1(*b*).

Table 2. g-Tensors [a] of W^V species detected during photolysis of $M_3[W(CN)_8]$ in non-aqueous solvents (0.01 mol dm^{-3}) at 293 K

Cation M	Solvent	Species (I)	Species (II)	Species (III)	Other species
K^+	$MeOH-H_2O$ (1:1)	1.9705		1.9482	
K^+	$MeOH-H_2O$ (2:1)	1.9705	1.9680	1.9472	1.918 (+0.002)
K^+ + crown ether	MeOH	1.9705	1.9660	1.9498 [b]	
PPh_4^+	MeOH	1.9701	1.9650	1.9486	1.9166
$AsPh_4^+$	MeCN	1.9702		1.9472	
$AsPh_4^+$	$Me_2SO-CH_2Cl_2$	1.9705			1.9371
$AsPh_4^+$	CH_2Cl_2	1.9705			1.9459
PPh_4^+	CH_2Cl_2			1.9472	
$AsPh_4^+$	Pyridine	1.9705 [c]	1.9539 [d]		

[a] ±0.0005. [b] a(W) = 61.4 G. [c] a(W) = 56.4 G. [d] a(W) = 56.4 G.

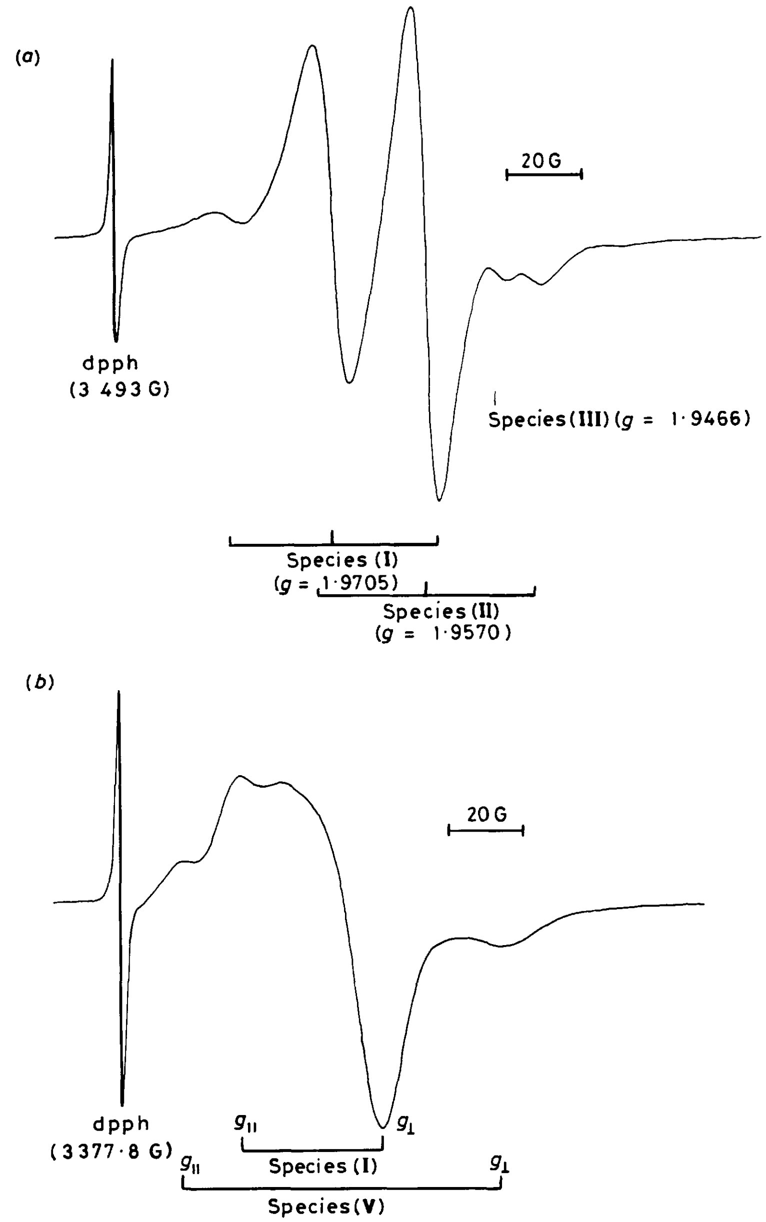


Figure 1. (*a*) E.s.r. spectrum of $[W(CN)_8]^{3-}$ in concentrated aqueous sodium azide (3.0 mol dm^{-3}) after 364 nm photolysis at 293 K. Field centre 3 520 G, field sweep 300 G; dpph = diphenylpicrylhydrazyl. (*b*) Post-photolysis (350—600 nm) e.s.r. spectrum at 77 K of $[W(CN)_8]^{3-}$ in concentrated aqueous sodium azide (3.0 mol dm^{-3}): photolysis at 293 K followed by freezing

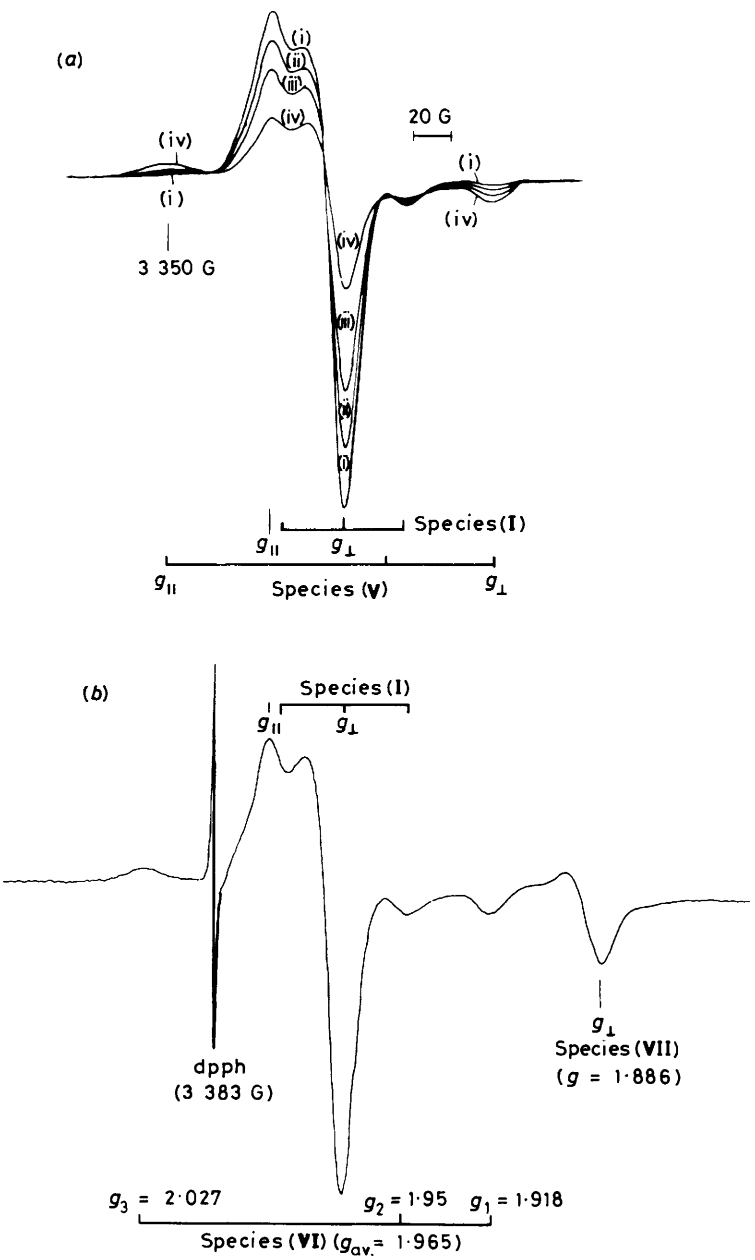


Figure 2. (*a*) E.s.r. spectra of $[AsPh_4]_3[W(CN)_8]$ in CH_2Cl_2 solution following photolysis at 77 K. Photolysis times: (i) 2, (ii) 6, (iii) 12, and (iv) 35 min. Field centre 3 340 G, field sweep 600 G. (*b*) E.s.r. spectrum after warming the solution in Figure 2(*a*) to 293 K and recooling to 77 K

Assignments for Species (**II**)—(**VII**).—The photolysis of $[W(CN)_8]^{3-}$ ion at 77 K in a variety of solvents leads to species (**V**) which is axially symmetric with $g_{av.} = 1.949$—1.953. On warming and recooling this is converted into species (**VI**) featuring full anisotropy with $g_{av.} = 1.966$—1.968 and species (**VII**) with $g_{\perp} = 1.883$—1.890. Our surmise is that the initial act of photolysis at 77 K (*i.e.* not referring to any photoredox process which would yield a diamagnetic W^{IV} species) is that of photodissociation to yield species (**V**) either as the co-ordinatively unsaturated $[W(CN)_7]^{2-}$ or such a species undergoing weak interaction with the water matrix, equation (3).

$$[W(CN)_8]^{3-} \xrightarrow[355\,\text{nm}]{h\nu} CN^- + [W(CN)_7]^{2-} \quad (3)$$
$$\text{(or } [W(CN)_7]^{2-}\cdots H_2O) \\ (\mathbf{V})$$

The warming–recooling experiment leads to species (**VI**) with a slightly larger average g-tensor: this we associate with the eight-co-ordinate species $[W(CN)_7(H_2O)]^{2-}$. Species (**VII**), with its greatly reduced $g_{\perp}$, we regard as a cyanide-bridged dimer $[(CN)_7W^{IV}(CN)W^{V}(CN)_7]^{6-}$ formed *via* equation (4).

$$\underset{(\mathbf{VI})}{[W^{V}(CN)_7(H_2O)]^{2-}} + [W^{IV}(CN)_8]^{4-} \longrightarrow \underset{(\mathbf{VII}),\ g_{\perp} = 1.883}{[(CN)_7W^{V}(CN)W^{IV}(CN)_7]^{6-}} \quad (4)$$

{The $[W(CN)_8]^{4-}$ will be present in solution as the product from the major photoredox pathway.} To consolidate this assignment we attempted to perform reaction (6), having first made $[W(CN)_7(H_2O)]^{3-}$ *via* reaction (5) (at pH 2 in $HClO_4$).[19]

Table 3. g-Tensors of W^V species detected during photolysis of $M_3[W(CN)_8]$ salts in frozen solutions at 77 K

								Products after warming and recooling to 77 K				
		Species (I)			Initial photoproduct [Species (V)]			Species (VI)				Species (VII)
Cation M	Solvent	$g_\perp$[a]	$g_\parallel$	$g_{av.}$	$g_\perp$	$g_\parallel$	$g_{av.}$	g_1	g_2	g_3	$g_{av.}$	$g_\perp$
$AsPh_4^+$	MeOH	1.965	1.980	1.970	1.918	2.010	1.949	1.918		2.019		1.890
K^+	H_2O–glycerol	1.968	1.982	1.972	1.919	2.013	1.950	1.920	1.957	2.027	1.968	
$AsPh_4^+$	MeCN	1.962	1.982	1.969	1.918	2.019	1.952	1.918		2.027		1.883
$AsPh_4^+$	Me_2SO	1.966	1.981	1.971	1.920	2.015	1.952	1.920		2.030		1.887
$AsPh_4^+$	Pyridine	1.965	1.978	1.919	1.918	2.016	1.951	1.918	1.955	2.025	1.966	1.885
$AsPh_4^+$	CH_2Cl_2	1.963	1.987	1.971	1.919	2.021	1.953	1.919		2.027		1.886
$AsPh_4^+$	CH_2Cl_2–PhMe (2:1 v/v)	1.963	1.977	1.968	1.918	2.012	1.950	1.918		2.027		1.888
K^+	H_2O[b] NaN_3 (3.0 mol dm^{-3})	1.963	1.985	1.970	1.945	1.994	1.962					

[a] ±0.002. [b] Solution photolysed at 293 K and frozen to 77 K.

Table 4. E.s.r. parameters* for the red and yellow solutions prepared by oxidation of photolysate of $[W^{IV}(CN)_8]^{4-}$ by $[W(CN)_8]^{3-}$

	Species (I)	Species (III)		Species (IV)		
Sample	g	g	a(W)	g	a(W)	Other species and comments
Red solution pH 2 ($HClO_4$)	1.9705	1.9469		1.9439	54.0	Species (III) is removed on addition of MeOH
Red solution + $K_3[W(CN)_8]$	1.9705	1.9465	63.5	1.9439		Complete conversion of (III) ⟶ (IV) after 3 h
Red solution + $K_3[Fe(CN)_6]$						g = 1.9398 (see text)
Yellow solution pH 2 ($HClO_4$)	1.9705			1.9449		
Yellow solution + Ce^{IV} + O_2	1.9705	1.9484				g = 1.9914, due to $[W(CN)_7(O_2)]^{2-}$
Yellow solution + H_2O_2	1.9705					g = 1.9914, due to $[W(CN)_7(O_2)]^{2-}$

* g Values ±0.0005; a values ±0.5 G.

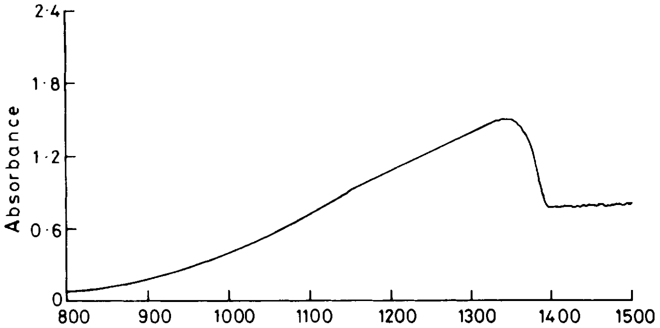


Figure 3. Electronic spectrum obtained on photolysis of $K_4[W(CN)_8]$ (0.005 mol dm^{-3}) in aqueous solution at pH 2.0 (adjusted with $HClO_4$) at 273 K using a 439 nm Balzer filter, followed by addition of an equimolar aliquot of $K_3[W(CN)_8]$. Path length 10 cm

$$[W^{IV}(CN)_8]^{4-} \xrightarrow[355\,\text{nm}]{h\nu} [W^{IV}(CN)_7(H_2O)]^{3-} + HCN \quad (5)$$

$$[W^{IV}(CN)_7(H_2O)]^{3-} + [W^V(CN)_8]^{3-} \longrightarrow [(CN)_7W^V(CN)W^{IV}(CN)_7]^{6-} + H_2O \quad (6)$$

Photolysis (365 nm) of $K_4[W(CN)_8]$ (0.01 mol dm^{-3}) at 0 °C (pH 2.0) resulted in production of a red solution ($\lambda_{max.}$ 510 nm) of the $[W^{IV}(CN)_7(H_2O)]^{3-}$ ion which was weakly paramagnetic with absorptions due to $[W(CN)_6]^{3-}$, species (**III**) (g = 1.9469) and (**IV**) (g = 1.9439) (see Table 4). This solution turned yellow in the dark over 3 h ($\lambda_{max.}$ 430, 1 350 nm), the intensity of the signal due to species (**IV**) increasing at the expense of that due to (**III**). Addition of an equimolar quantity of $K_3[W(CN)_8]$ to the red solution produced the same optical and e.s.r. spectral changes instantly. The yellow solution (Table 4) showed remarkable colour changes on cooling, equation (7).

$$\underset{[\lambda_{max.}\ 1\,350,\ 1\,100\,(\text{sh}),\ 430\ \text{nm}]}{\underset{(293\ \text{K})}{\text{Yellow solution}}} \underset{\text{warm}}{\overset{\text{cool}}{\rightleftharpoons}} \underset{(259\ \text{K})}{\text{Blue solution}} \quad (7)$$

The observation in the yellow solution of an intense near-i.r. band is consistent with an assignment of species (**IV**) to the mixed-valence dimer [to which the low-temperature species (**VII**) has also been assigned]. This assignment is supported by the intensification of the near-i.r. band on addition of $[W(CN)_8]^{3-}$ to either the red or the yellow solution (Figure 3); addition of $[W(CN)_8]^{3-}$ to the red solution produces the material with g = 1.9465 (Figure 4). The striking colour change with temperature is considered to be due simply to a temperature dependence of the band rather than to perturbation of an equilibrium between yellow and blue species. The blue colouration was apparent only in partly frozen samples (preventing optical measurements); addition of LiCl or glycerol as freezing-point depressants resulted in a loss of the blue colour, although there was a small hypsochromic shift of the near-i.r. band.

The e.s.r. spectra of the red and yellow solutions suggest that species (**III**) is $[W(CN)_7(H_2O)]^{2-}$ while species (**IV**) is the mixed-valence dimer. In support of the assignment to species (**III**) is the observation that addition of $[Fe(CN)_6]^{3-}$ to the 'red solution' produced a species with g = 1.9398 assigned to the mixed-valence dimer $[(CN)_5Fe(CN)W(CN)_7]^{6-}$. Again, when oxidants such as Ce^{IV}, H_2O_2, or $S_2O_8^{\ 2-}$ are added to either the red or yellow solutions, then only $[W(CN)_8]^{3-}$ is formed provided the solutions are O_2-free. If oxygen is present then a

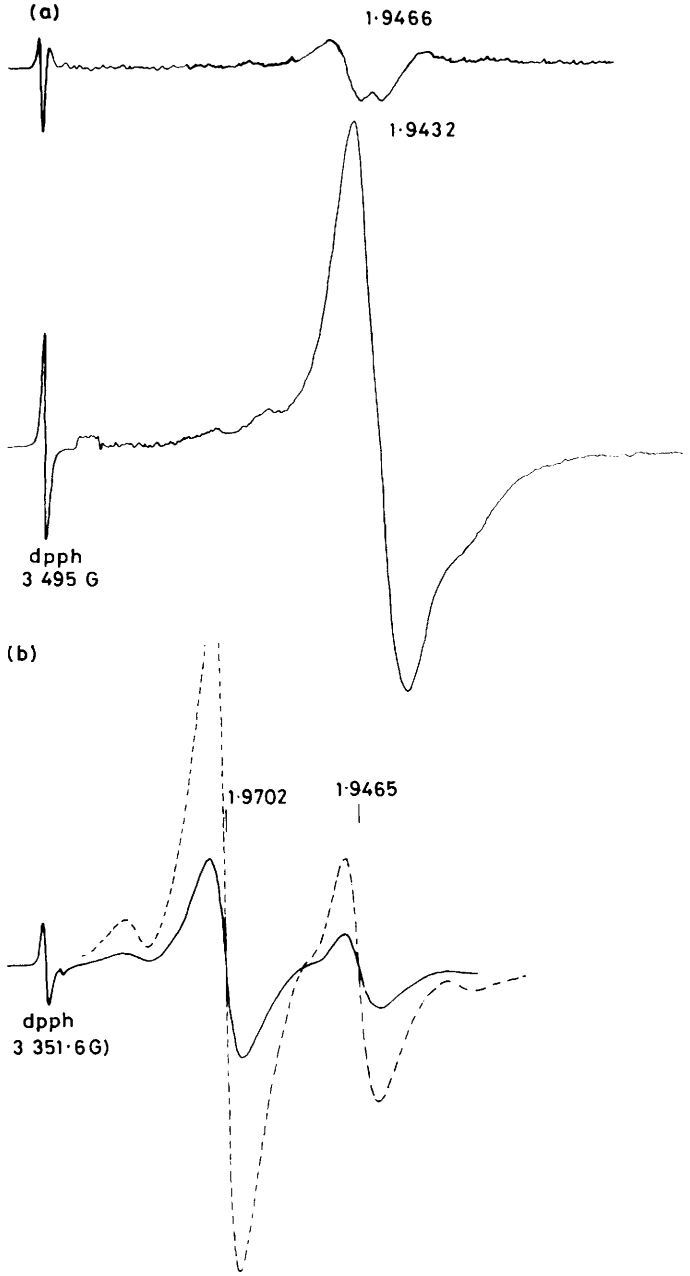


Figure 4. (*a*) E.s.r. spectrum (with second derivative) of the red solution obtained on 439 nm photolysis of aqueous $[W(CN)_8]^{4-}$ ions at pH 2. (*b*) (——) E.s.r. spectrum of the solution in (*a*) after addition of $K_3[W(CN)_8]$; (---) same spectrum at higher gain (× 3.5)

remarkably narrow-line spectrum is produced at $g = 1.9914$ (Figure 5) which we assign to $[W^V(CN)_7(OO^{\bullet})]^{2-}$. (This formulation is the W^V analogue of the 535 nm species claimed by Sieklucka *et al.*[7]) The narrow, low-field line ($g = 2.0125$) found in the Ce^{IV} oxidation is probably due to a peroxocerium species: many examples of these have been reported, *e.g.* for Ti^{IV} ($g = 2.0165$)[20] and Co^{III} ($g = 2.0147$).[21]

These assignments prompted an experiment in which a mixture of $[W(CN)_8]^{3-}$ and $[W(CN)_8]^{4-}$ was irradiated with light passed through a 439 nm interference filter, *i.e.* that which is absorbed only by $[W(CN)_8]^{4-}$. Under these conditions, $[W(CN)_7(H_2O)]^{3-}$, which is produced *via* reaction (5), undergoes reaction (8); $[W(CN)_7(H_2O)]^{2-}$ displays $g = 1.947$.

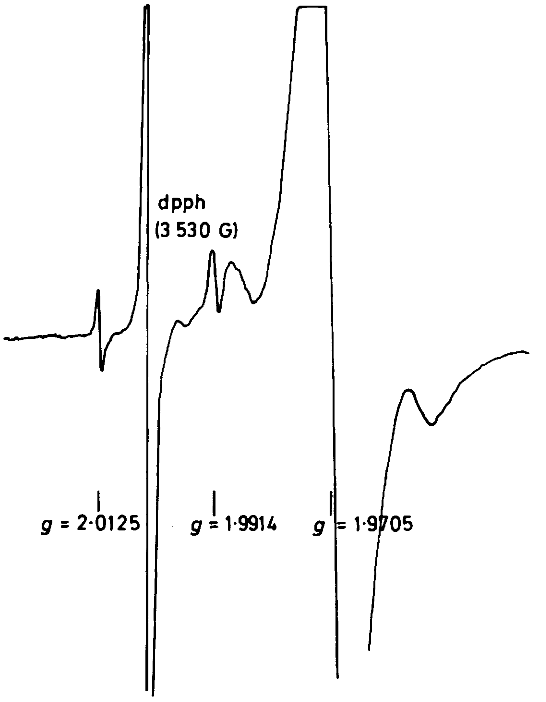
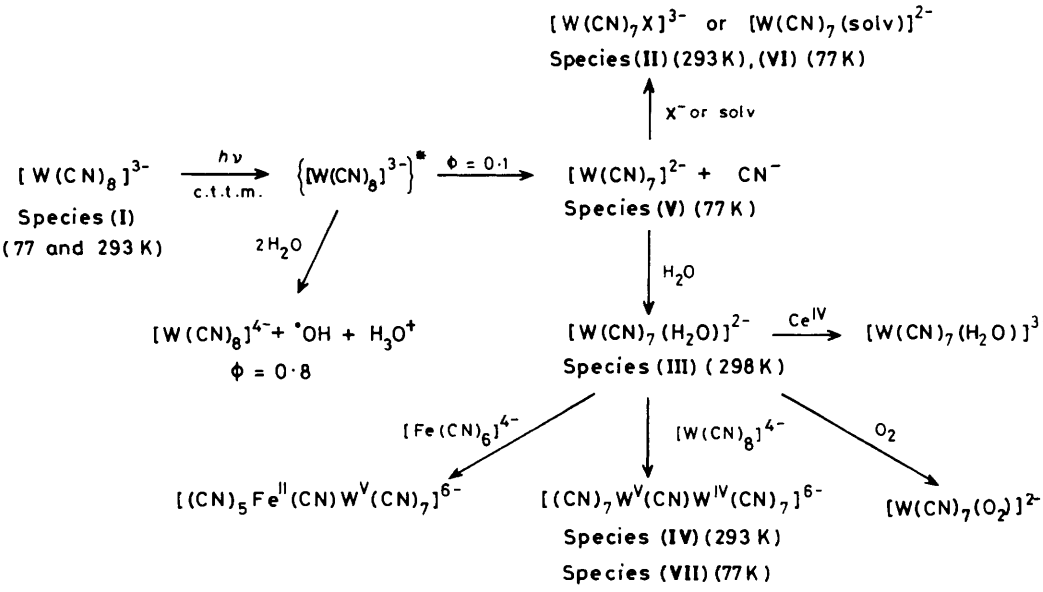


Figure 5. E.s.r. spectrum of the red solution after treatment with Ce^{IV} in the presence of oxygen. The resonances centred at $g = 2.0125$, 1.9914, and 1.9705 are due, respectively, to a peroxocerium species, $[W(CN)_7(OO^{\bullet})]$, and $[W(CN)_8]^{3-}$

$$[W^{IV}(CN)_7(H_2O)]^{3-} + [W(CN)_8]^{3-} \longrightarrow [W(CN)_7(H_2O)]^{2-} + [W(CN)_8]^{4-} \quad (8)$$

Reaction (8) also occurs in MeOH and MeOH–H_2O mixtures but not in Me_2SO, CH_2Cl_2, or MeCN when the salt $[AsPh_4]_3[W(CN)_8]$ is used. Considering the relationship between our assignments and those made previously by Sieklucka *et al.*[7] who claim that their species with $g = 1.943$ is $[W(CN)_7(H_2O)]^{2-}$, our inclination is to assign these species to the mixed-valence dimer, for which we find $g = 1.9439$. The remaining question with regard to fluid solutions concerns the dominant species (**II**) ($g = 1.9524$—1.9596) formed during photolysis at room-temperature in the presence of large concentrations of N_3^-, Cl^-, or SCN^- ions in aqueous solution and also in pyridine (py) as solvent. This species is *not* formed during photolysis of such solutions at 77 K. A clue to the nature of species (**II**) comes from the spectrum produced on photolysis of $[W(CN)_8]^{3-}$ in the presence of KBr (3.0 mol dm^{-3}): in this case a species (**II**)-type signal is found at $g = 1.9798$ with hyperfine splitting $a(^{79,81}Br)$ (unresolved) = 11.9 G (Table 1). The g-shift and $a(^{79,81}Br)$ point to the $[W(CN)_7Br]^{3-}$ ion, implying assignment of structure $[W^V(CN)_7X]^{n-}$ (X = Cl, N_3, or py) to species (**II**). {Addition of KI (2.0 mol dm^{-3}) to $[W(CN)_8]^{3-}$ led to thermal reduction of W^V but some species (**III**) was formed.} Photolysis in the presence of KSCN yielded *two* species (**II**)-type signals (Table 1); that at $g = 1.9524$ is attributed to $[W(CN)_7(NCS)]^{3-}$ while that at $g = 1.9652$ is considered to be the isomer, $[W(CN)_7(SCN)]^{3-}$. Photolysis of $[W(CN)_8]^{3-}$ in the presence of $NaNO_2$ (1.0 mol dm^{-3}) yielded a low-field species with $g = 2.0006$ and $a(^{14}N) = 13.5$ G which we believe to be $[W(CN)_7(NO)]^{3-}$ rather than $[W(CN)_7(NO_2)]^{3-}$. Finally, photolysis in the presence of sodium formate (3.0 mol dm^{-3}) yields only species (**III**) but $CO_2^{\bullet -}$ radicals could be spin-trapped.

Interestingly, photolysis in the presence of high concentr-



Scheme. φ = Quantum yield

ations of certain salts (KBr, KCl, LiCl, NaN_3, $NaClO_4$) afforded higher concentrations of species (**IV**) (the dimer) than simple aqueous solutions.

In the non-aqueous solutions at ambient temperatures, species (**II**) is (by analogy with aqueous media containing high concentrations of co-ordinating anions) $[W^V(CN)_7(solv)]^{2-}$ (solv = MeOH, Me_2SO, or py), while species (**III**) is $[W^V(CN)_7(H_2O)]^{2-}$, produced by reaction of $[W(CN)_7]^{2-}$ with adventitious traces of water. The role of traces of water is indicated vividly from the photolysis of $[PPh_4]_3[W(CN)_8]$ in MeCN in the presence of *N*-(benzylidene)-t-butylamine *N*-oxide when the spin-adduct of ·OH was observed; moreover, when rigorously dried MeCN was employed, no photoredox process occurred. Species (**V**) initially produced in organic solvents at 77 K is assigned as $[W(CN)_7]^{2-}$; that formed after warming and recooling [species (**VI**)] is attributed to $[W(CN)_7(solv)]^{2-}$, *i.e.* the same as species (**II**) found in solution, while species (**VII**) ($g_\perp = 1.89$) is assigned to the bridged dimer, *i.e.* the same as species (**IV**) found in aqueous solution. The photoreactions of $[W(CN)_8]^{3-}$ as evidenced from our various data, together with the array of intermediates and products, are summarised in the Scheme. The initial intermediate is given as $[W(CN)_7]^{2-}$ rather than $[W(CN)_7(H_2O)]^{2-}$: there is some e.s.r. evidence for discrimination between these two and whereas the photolysis of glassy solutions of $[W(CN)_8]^{3-}$ at 77 K produces a yellow-brown colouration, the process of slight warming and recooling to 77 K, when $[W(CN)_7(H_2O)]^{2-}$ is formed, is accompanied by a colour change to reddish purple.

Further strong evidence for $[W(CN)_7]^{2-}$ as a free entity in non-aqueous media comes from photolysis of $[PPh_4]_3[W(CN)_8]$ in MeCN–benzene (5:1 v/v) in the presence of nitrosodurene when a spin-trap product was observed with $a(^{14}N) = 9.59$ G which we attribute to $[C_6Me_4H\text{-}N(O^\cdot)\text{-}W(CN)_7]^{2-}$, by analogy with its Mo counterpart.[8]

Acknowledgements

We thank the British Council (G.D.R. office), the University of Warwick (Research and Innovations Fund), and the Karl-Marx-Universität (Leipzig) for supporting the study visit of D. R. to the U. K. Professor H. Hennig of K.M.U. is thanked for his encouragement. We thank Mr. A. D. Wright (Warwick) for his assistance in performing preliminary experiments on the photochemical e.s.r. study of $[W(CN)_8]^{3-}$ ions in organic solvents as part of his third-year undergraduate project and Dr. Barbara Sieklucka who measured u.v.–visible spectra of $[PPh_4]_3[W(CN)_8]$ in organic solvents.

References

1 B. Sieklucka, A. Kanas, and A. Samotus, *Transition Met. Chem.*, 1982, **7**, 131.
2 V. Carassiti and V. Balzani, *Ann. Chim.* (*Rome*), 1961, **51**, 518; V. Balzani and A. Carassiti, *ibid.*, p. 533.
3 A. Samotus, *Rocz. Chem.*, 1973, **47**, 265.
4 G. W. Gray and J. T. Spence, *Inorg. Chem.*, 1971, **10**, 2751.
5 Z. Stasicka and H. Bulska, *Rocz. Chem.*, 1974, **48**, 389; A. Marchaj, A. Plesinski, and Z. Stasicka, *ibid.*, 1976, **50**, 1239.
6 D. Rehorek, E. G. Janzen, and H. J. Stronks, *Z. Chem.*, 1982, **22**, 64.
7 B. Sieklucka, A. Samotus, S. Sostero, and O. Traverso, *Inorg. Chim. Acta*, 1984, **86**, L51.
8 D. Rehorek, J. Salvetter, A. Hantschmann, H. Hennig, Z. Stasicka, and A. Chodkowska, *Inorg. Chim. Acta*, 1979, **37**, L471.
9 D. Rehorek and E. G. Janzen, *Z. Chem.*, 1985, **25**, 451.
10 D. Rehorek and H. Hennig, *Can. J. Chem.*, 1982, **60**, 1565.
11 K. R. Butter, T. J. Kemp, B. Sieklucka, and A. Samotus, *J. Chem. Soc., Dalton Trans.*, 1986, 1217.
12 A. Samotus and B. Sieklucka, *J. Inorg. Nucl. Chem.*, 1978, **40**, 315.
13 R. A. Pribush and R. D. Archer, *Inorg. Chem.*, 1974, **13**, 2556; P. M. Kiernan and A. P. Griffith, *J. Chem. Soc., Dalton Trans.*, 1975, 2489.
14 B. R. McGarvey, *Inorg. Chem.*, 1966, **5**, 476.
15 J. G. Leupoldt, L. D. C. Bok, and J. Cilliers, *Z. Anorg. Allg. Chem.*, 1974, **407**, 350.
16 L. I. Smith and F. L. Taylor, *J. Am. Chem. Soc.*, 1935, **57**, 2460.
17 F. D. Greene and J. F. Pazos, *J. Org. Chem.*, 1969, **34**, 2269.
18 H. B. Ambroz and T. J. Kemp, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1420.
19 A. Samotus and B. Sieklucka, *J. Inorg. Nucl. Chem.*, 1978, **40**, 315; B. Sieklucka and A. Samotus, *ibid.*, 1980, **42**, 1003.
20 M. S. Bains, J. C. Arthur, jun., and O. Hinojosa, *J. Phys. Chem.*, 1968, **72**, 2250.
21 A. Tkáč, K. Veselý, and L. Omelka, *J. Phys. Chem.*, 1971, **75**, 2575.

Received 19*th December* 1986; *Paper* 6/2444