Tungsten(VI) Complexes as New Products in the High-intensity Photolysis of Octacyanotungstate(V) Ion in Hydroxylic Solvents; Crystal Structure of $[PPh_4]_2[W(CN)_6O]\cdot H_2O$ and $[PPh_4]_2[W(CN)_5O(OMe)]$†

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Irradiation of octacyanotungstate(V) ion under high light intensities leads to new photoproducts based on W^{VI} not found at normal intensities. In water, the $[W(CN)_6O]^{2-}$ ion is formed while in water–methanol (1 : 1 v/v) the $[W(CN)_5O(OMe)]^{2-}$ ion is produced on standing after photolysis. The formation of these unexpected products is viewed as proceeding *via* a two-quantum process. The ions, in the form of their $[PPh_4]^+$ salts [(**1**) and (**2**) respectively], were structurally characterized by *X*-ray diiffraction as pentagonal bipyramids with five equatorial cyanide ligands. For (**1**), R = 0.028 for 6 786 unique observed $[I/\sigma(I) \geqslant 3.0]$ reflections, and for (**2**), R = 0.051 for 6 865 unique observed $[I/\sigma(I) \geqslant 2.0]$ reflections. For both compounds, W=O is 1.693(2) (mean), W–C (equatorial) is 2.167(24), W–C (axial) is 2.277(3), and W–O(Me) (axial) is 1.906(9) Å.

On irradiation into its charge-transfer-to-metal (c.t.t.m.) band, octacyanotungstate(V) ion undergoes photolysis in aqueous solution at normal light intensities by a c.t.t.m. process involving a molecule of solvent [equation (1)].[1,2] The same general process occurs in some non-aqueous solvents.[3] Reaction (1) has a quantum yield of *ca.* 0.8 over a wide pH range.[2] Sieklucka *et al.*[4] showed that at high light intensities a new, red-purple photoproduct is formed ($\lambda_{max.}$ 535 nm) which was attributed to the $[W^{IV}(CN)_7(O_2)]^{3-}$ ion on the basis of its Raman spectrum. Photolysis in methanol–water (1:1 v/v) also produces this product, which changes to a deep violet material ($\lambda_{max.}$ 560 nm) on standing, attributed to $[(NC)_7WO_2W(CN)_7]^{6-}$ ion.[4]

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

In the present paper, we show that new photoproducts can be isolated from the high-intensity photolysate consisting of pentagonal-bipyramidal oxo-anions based on W^{VI}, as demonstrated by *X*-ray structural analysis. A preliminary account of this work has appeared.[5]

Experimental

Irradiation.—This was carried out with the focused output of a 200-W point-source high-pressure xenon–mercury lamp supplied by Wotan and mounted in a housing equipped with condensing lenses on an optical bench. The unfiltered lamp output of *ca.* 5×10^{17} quanta s^{-1} was passed into the 1-cm optical quartz cell which was cooled by circulating water. The same products could be obtained using a Pyrex filter ($\lambda_{trans.} > 310$ nm) but after longer photolysis times.

Materials.—The preparation of $K_3[W(CN)_8]\cdot 1.5H_2O$ has been described previously.[6] The purity of the complex was checked spectrophotometrically (i.r. and u.v.–visible spectra). Tetraphenylphosphonium chloride PPh_4Cl (Aldrich) was used as received. Methanol and acetonitrile (Merck, Uvasol) were used without further purification. Thin-layer chromatography (t.l.c.) was performed by using aluminium sheets coated with 0.2 mm thick silica gel 60 (Merck). Water was doubly distilled.

Characterization Methods.—Infrared spectra of new complexes were recorded on a Perkin-Elmer model 580 B spectrophotometer, Raman spectra on a Jobin-Yvon model HG2S Ramanor spectrophotometer equipped with a SP model 71 argon-ion laser (Spectra Physics). Fast atom bombardment (f.a.b.) mass spectra were obtained on a MS 80 mass spectrometer fitted with a f.a.b. gun (Kratos Analytical Instruments) and data were analysed using a DS 90 data system. The primary xenon beam energy was 8 keV (*ca.* 1.3×10^{-17} J) with a gun current of 1 mA and the spectra were recorded using an unheated sample probe at a resolution of *ca.* 1 000. Complexes were examined in a matrix of 3-nitrobenzyl alcohol.

Proton n.m.r. spectra were measured on a Bruker model WH 400 Fourier-transform instrument with 3-trimethylsilylpropanesulphonic acid (sodium salt) as internal standard. Elemental analyses were obtained from Butterworth Laboratories Ltd.

Synthesis of $[PPh_4]_2[W(CN)_6O]\cdot H_2O$ (**1**).—This was obtained as a major by-product in the form of the potassium salt in the preparation of $[PPh_4]_2[W(CN)_5O(OMe)]$ (see below) but it was also prepared by photolysis of potassium octacyanotungstate(V) (2.5 mmol, 1.3 g) in aqueous solution (250 cm^3, 0.010 mol dm^{-3}) with the 200-W source (bare arc), using a series of aliquots (3 cm^3) placed in a 1-cm quartz spectrophotometer cell. The combined photolysate ($\lambda_{max.}$ 537 nm) was treated with methanolic PPh_4Cl (0.02 mol dm^{-3}, 5

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† Bis(tetraphenylphosphonium) hexacyano-oxotungstate(VI) hydrate and bis(tetraphenylphosphonium) pentacyano(methoxo)oxotungstate(VI).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Atom co-ordinates (× 10^4) for $[PPh_4]_2[W(CN)_6O]\cdot H_2O$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	3 428.7(2)	1 904.8(1)	2 181.8(1)	C(135)	2 436(6)	75(4)	−1 797(3)
P(1)	5 480.7(10)	1 952.2(7)	−1 650.8(6)	C(136)	3 355(5)	707(4)	−1 980(3)
P(2)	9 241.5(10)	6 669.6(7)	3 779.2(6)	C(141)	7 007(4)	1 907(3)	−1 107(2)
O	3 735(3)	808(2)	1 618(2)	C(142)	7 143(4)	2 369(3)	−266(3)
C(1)	2 925(4)	3 350(3)	2 965(2)	C(143)	8 289(5)	2 322(4)	164(3)
N(1)	2 638(4)	4 062(2)	3 347(2)	C(144)	9 293(5)	1 822(4)	−237(4)
C(2)	2 522(4)	1 474(3)	3 209(3)	C(145)	9 168(5)	1 359(4)	−1 067(4)
N(2)	2 059(4)	1 262(2)	3 772(2)	C(146)	8 020(4)	1 398(3)	−1 506(3)
C(3)	4 880(4)	1 896(3)	3 147(3)	C(211)	7 635(4)	6 191(2)	3 913(2)
N(3)	5 630(4)	1 812(3)	3 636(3)	C(212)	6 960(4)	5 602(3)	3 245(2)
C(4)	5 163(5)	2 648(3)	1 903(3)	C(213)	5 703(4)	5 280(3)	3 351(2)
N(4)	6 093(4)	3 038(3)	1 761(3)	C(214)	5 109(4)	5 556(3)	4 112(2)
C(5)	2 950(5)	2 566(3)	1 174(3)	C(215)	5 786(4)	6 151(3)	4 775(2)
N(5)	2 667(5)	2 914(3)	642(3)	C(216)	7 043(4)	6 467(3)	4 682(2)
C(6)	1 350(5)	1 766(3)	1 953(3)	C(221)	9 848(4)	6 034(3)	2 794(2)
N(6)	227(4)	1 658(4)	1 820(3)	C(222)	9 973(4)	5 058(3)	2 656(3)
C(111)	5 734(4)	1 657(3)	−2 769(2)	C(223)	10 393(5)	4 555(4)	1 889(3)
C(112)	5 867(4)	725(3)	−3 179(3)	C(224)	10 669(5)	5 005(4)	1 271(3)
C(113)	6 094(5)	498(3)	−4 026(3)	C(225)	10 521(5)	5 965(4)	1 392(3)
C(114)	6 170(4)	1 194(3)	−4 464(3)	C(226)	10 112(4)	6 481(3)	2 156(3)
C(115)	6 031(4)	2 119(3)	−4 064(3)	C(231)	10 315(4)	6 621(3)	4 645(2)
C(116)	5 805(4)	2 360(3)	−3 216(2)	C(232)	11 226(4)	5 923(3)	4 606(3)
C(121)	4 913(4)	3 137(3)	−1 347(2)	C(233)	11 978(4)	5 924(3)	5 307(3)
C(122)	5 790(5)	3 901(3)	−1 341(3)	C(234)	11 838(4)	6 583(3)	6 036(3)
C(123)	5 351(5)	4 800(3)	−1 176(3)	C(235)	10 932(5)	7 263(3)	6 077(3)
C(124)	4 052(6)	4 946(3)	−1 005(3)	C(236)	10 186(4)	7 298(3)	5 386(3)
C(125)	3 212(5)	4 200(3)	−997(3)	C(241)	9 122(4)	7 900(2)	3 790(2)
C(126)	3 624(4)	3 292(3)	−1 173(3)	C(242)	10 260(4)	8 448(3)	3 772(3)
C(131)	4 289(4)	1 124(3)	−1 405(2)	C(243)	10 198(5)	9 402(3)	3 826(3)
C(132)	4 272(5)	918(3)	−630(3)	C(244)	9 022(5)	9 824(3)	3 911(3)
C(133)	3 324(5)	281(3)	−461(3)	C(245)	7 890(5)	9 295(3)	3 938(3)
C(134)	2 439(5)	−154(3)	−1 045(3)	C(246)	7 938(4)	8 326(3)	3 869(2)

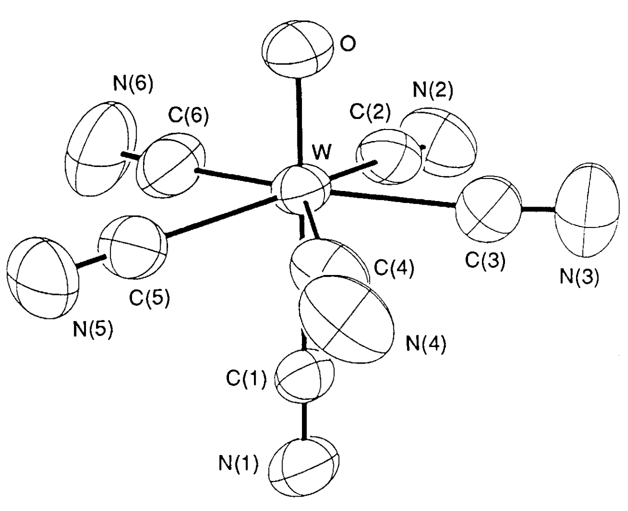


Figure 1. View of the anion $[W(CN)_6O]^{2-}$ in crystalline $[PPh_4]_2[W(CN)_6O]\cdot H_2O$

mmol, 1.9 g) at 0 °C. The almost colourless (palest pink) solid was recovered, washed several times with water and finally with diethyl ether, and recrystallized from methanol at 4 °C (Found: C, 61.50; H, 4.00; N, 8.00; W, 17.60. Calc. for $C_{54}H_{42}N_6O_2P_2W$: C, 61.60; H, 4.00; N, 8.00; W, 17.45%). Yield 0.08 g (3%). Significant i.r. frequencies (in addition to bands characteristic for PPh_4^+) are: ν(OH) 3 420—3 560w (br); ν(CN) 2 143w, 2 159w, and 2 206m; δ(HOH) 1 620w (br); ν(W=O) 963vs cm^{-1}. Raman (argon-ion laser, 514.5 nm): ν(CN) 2 141m, 2 159vs, and 2 163s; ν(W=O) 961vs cm^{-1}. F.a.b. mass spectrum (negative ion): *m/z* 823 (27), $[M + 3\text{-}O_2NC_6H_4OH - PPh_4 - CN]^-$; 697 (100), $[M - PPh_4]^-$; and 673 (11%), $[M - PPh_4 - CN]^-$. For a pentagonal bipyramidal species of C_{5v} symmetry there should be three i.r.-active modes ($2A_1 + 1E_1$) in the ν_{sym}(C≡N) region and four Raman-active modes ($2A_1 + 1E_1 + 1E_2$); one of the predicted Raman frequencies appears only as a shoulder on the band at 2 141 cm^{-1} for our solid-state sample.

Crystal-structure Analysis of Complex (**1**).—*Crystal data.* $C_{54}H_{42}N_6O_2P_2W$, $M = 1\,052.7$, triclinic, space group $P\bar{1}$, $a = 10.247(2)$, $b = 14.510(3)$, $c = 16.394(3)$ Å, $\alpha = 103.19(2)$, $\beta = 90.78(1)$, $\gamma = 92.21(2)°$, $U = 2\,370.8(7)$ Å^3, $Z = 2$, $D_c = 1.46$ g cm^{-3}, Mo-*K* radiation ($\lambda = 0.710\,69$ Å), μ(Mo-*K*) = 26.8 cm^{-1}, $T = 290$ K, $F(000) = 1\,036$, $R = 0.028$ for 6 786 unique observed reflections $[I/\sigma(I) > 3]$.

Crystals obtained as irregular very pale pink flakes from MeOH (NB. The colour is due to a trace impurity removable by t.l.c.). Data were collected with a Syntex $P2_1$ four-circle diffractometer in ω—2θ mode. Maximum 2θ was 50°, with scan range ±0.95° (2θ) around the $K_{\alpha_1} - K_{\alpha_2}$ angles, scan speed 4—29° min^{-1}, depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for 0.25 for the scan time. The *hkl* ranges were 0—2, −16 to +16, and −18 to +18. Three standard reflections were monitored every 200 reflections, and showed slight changes during data collection: the data were rescaled to correct for this. Density was measured by flotation. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ($24 < 2\theta < 26°$). Reflections were processed using profile analysis to give 8 347 unique reflections ($R_{int} = 0.015$); 6 786 were considered observed $[I/\sigma(I) \geqslant 3.0]$ and used in refinement; they were corrected for Lorentz, polarization, and absorption effects, the last by the Gaussian method;[7] maximum and minimum transmission factors were 0.82 and 0.43. Crystal dimensions were

Table 2. Principal bond lengths (Å) and angles (°) for $[PPh_4]_2[W(CN)_6O]\cdot H_2O$

W–O	1.691(3)	W–C(1)	2.277(3)
W–C(2)	2.137(4)	W–C(3)	2.159(4)
W–C(4)	2.152(5)	W–C(5)	2.151(5)
W–C(6)	2.151(5)	C(1)–N(1)	1.131(5)
C(2)–N(2)	1.142(6)	C(3)–N(3)	1.132(6)
C(4)–N(4)	1.144(7)	C(5)–N(5)	1.143(7)
C(6)–N(6)	1.167(7)		
O–W–C(1)	177.1(1)	O–W–C(2)	97.0(1)
O–W–C(4)	98.8(2)	O–W–C(3)	94.7(1)
O–W–C(5)	99.4(1)	O–W–C(6)	95.3(2)
W–C(2)–N(2)	178.2(3)	W–C(1)–N(1)	178.1(3)
W–C(4)–N(4)	179.2(5)	W–C(3)–N(3)	174.4(4)
W–C(6)–N(6)	177.7(4)	W–C(5)–N(5)	178.5(5)

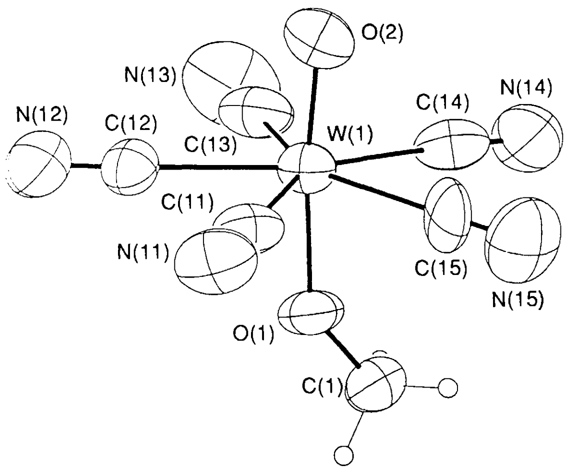


Figure 2. View of one of the two independent anions $[W(CN)_5O(OMe)]^{2-}$ in crystalline $[PPh_4]_2[W(CN)_5O(OMe)]$

0.41 × 0.22 × 0.077 mm, with principal bounding faces 101 and $\bar{1}0\bar{1}$. No systematic absences. The heavy atom was located by the Patterson interpretation section of SHELXTL and the light atoms then found on successive Fourier syntheses.

Anistropic thermal parameters were used for all non-H atoms. Hydrogen atoms were given fixed isotropic thermal parameters, $U = 0.07$ Å^2. Those defined by the molecular geometry were inserted at calculated positions and not refined; final refinement was on F by cascaded least-squares methods. Largest positive and negative peaks on a final Fourier difference synthesis were of height +0.8 and −0.5 e Å^{-3}.

A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.000\,35$ was used and shown to be satisfactory by a weight analysis. Final $R = 0.028$, $R' = 0.029$. Maximum shift/error in final cycle 0.1. Computing was with SHELXTL[7] on a Data General DG30. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 8. The structure is shown in Figure 1, final atomic co-ordinates are given in Table 1, and selected bond lengths and angles in Table 2.

Synthesis of $[PPh_4]_2[W(CN)_5O(OMe)]$ (**2**).—Aliquots (3 cm^3) of potassium octacyanotungstate(V) in aqueous methanol (1 : 1 v/v; 0.010 mol dm^{-3}) were irradiated (bare arc) for 3 min until a total of 250 cm^3 of solution (1.3 g, 2.5 mmol of solute) had been so treated. The collected irradiated solution ($\lambda_{max.}$ 537 nm) was left in the dark for 48 h to allow conversion of the product ($\lambda_{max.}$ 537 nm) into a deep violet species ($\lambda_{max.}$ 560 nm). Afterwards the solution was kept for 24 h at −30 °C, when $K_2[W(CN)_6O]$ was deposited; this was filtered off and to the filtrate PPh_4Cl (0.01 mol, 3.74 g) in water–methanol (1 : 1 v/v) (20 cm^3) was added. After standing for 24 h at −30 °C, the crude violet solid was filtered off, washed with much water and finally with diethyl ether. The solid sample was dissolved in the minimum amount of MeOH and separated on t.l.c. silica gel 60 plates with MeCN as eluant. The first, colourless fraction ($R_f = 0.62$) was recovered, dissolved in MeOH, filtered, and recrystallized at room temperature (Found: C, 62.15; H, 4.30; N, 6.70. Calc. for $C_{54}H_{43}N_5O_2P_2W$: C, 62.40; H, 4.15; N, 6.75%). Yield 0.04 g (1.5%). I.r. (in addition to bands characteristic for PPh_4^+): ν(OH) 3 475—3 535m (br), 3 070m; ν_{sym}-, ν_{asym}-(CH_3) 2 825s, 2 920s; ν(CN) 2 164m, 2 206w; δ(HOH) 1 640w (br); ν(CO) 1 080s (sh) (partly masked by PPh_4^+); ν(W=O) 933vs; ν(W–O) 540 (partly masked by PPh_4^+); ν(W–CN) 495s; δ(W–CN) 277m, 368vs, and 418s cm^{-1}). ^{1}H N.m.r. (CD_3CN): δ 3.61 (OMe) (intensity ratio gives one OMe for two PPh_4^+). F.a.b. mass spectrum (negative ion): m/z 822 (100), $[M + 3\text{-}O_2NC_6H_4OH - PPh_4 - OMe]^-$; 701 (23), $[M - PPh_4]^-$; 483 (9), $[M + 3\text{-}O_2NC_6H_4OH - 2PPh_4 - OMe]^-$; 456 (67), $[M + 3\text{-}O_2NC_6H_4OH - 2PPh_4 - OMe - CN]^-$; and 428 (24%), $[M + 3\text{-}O_2NC_6H_4OH - 2PPh_4 - OMe - 2CN]^-$.

Crystal-structure Analysis of Complex (**2**).—*Crystal data.* $C_{54}H_{43}N_5O_2P_2W$, $M = 1\,039.7$, triclinic, space group $P\bar{1}$, $a = 10.713(3)$, $b = 19.208(5)$, $c = 24.787(6)$ Å, $\alpha = 99.17(2)$, $\beta = 90.64(2)$, $\gamma = 99.40(2)°$, $U = 4\,964(2)$ Å^3, $Z = 4$, $D_c = 1.37$ g cm^{-3}, Mo-K radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K) = 24.8 cm^{-1}, $T = 298$ K, light violet blocks. (NB. The colour is now known to be due to a trace impurity, removable by t.l.c.).

Data were collected as for complex (**1**). Maximum 2θ was 45° with scan range ±0.95° (2θ around the $K_{\alpha_1} - K_{\alpha_2}$ angles), scan speed 4.5—29° min^{-1}, depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 200 reflections, and showed a moderate decrease during data collection. The data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ($18 < 2\theta < 20°$). Reflections were processed using profile analysis to give 12 962 unique reflections; 6 865 were considered observed [$I/\sigma(I) \geqslant 2.0$] and used in refinement; they were corrected as for complex (**1**). Maximum and minimum transmission factors were 0.75 and 0.68. Crystal dimensions were 0.26 × 0.30 × 0.16 mm. No systematic absences. Heavy atoms were located by the Patterson interpretation section of SHELXTL[7] and the light atoms then found on successive Fourier syntheses. Despite the relatively deep purple colour of this particular sample, no trace was seen of partial substitution by a second species. Assignment of thermal parameters and treatment of the hydrogen atoms as for complex (**1**). Methyl groups were treated as rigid units, with their initial orientation taken from the strongest H-atom peaks on a Fourier difference synthesis. Final refinement was on F by least-squares methods refining 722 parameters. Largest positive and negative peaks on a final Fourier difference synthesis were of height 0.9 and −0.8e Å^{-3}. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.0015$ was used and shown to be satisfactory by a weight analysis. Final $R = 0.051$, $R' = 0.061$. Maximum shift/error in final cycle 0.2. Computing with SHELXTL PLUS[7] on a DEC Microvax-II. Source of scattering factors and anomalous dispersion factors as for complex (**1**). The structure is shown in Figure 2, final atomic co-ordinates are given in Table 3, and selected bond lengths and angles in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles, for both structures.

Table 3. Atomic co-ordinates (× 10^4) for $[PPh_4]_2[W(CN)_5O(OMe)]$

Atom	*x*	*y*	*z*
W(1)	2 722.0(5)	6 469.6(3)	2 625.2(2)
O(1)	2 532(8)	5 545(4)	2 845(3)
C(1)	2 367(13)	4 814(7)	2 644(5)
O(2)	2 891(8)	7 235(5)	2 351(3)
C(11)	4 284(13)	6 858(7)	3 220(6)
N(11)	5 121(12)	7 076(7)	3 537(5)
C(12)	1 950(13)	6 914(7)	3 384(6)
N(12)	1 541(13)	7 160(7)	3 776(5)
C(13)	710(17)	6 323(8)	2 518(6)
N(13)	−371(14)	6 224(9)	2 454(6)
C(14)	2 157(15)	5 847(8)	1 816(7)
N(14)	1 867(13)	5 494(7)	1 404(5)
C(15)	4 414(16)	6 199(8)	2 246(6)
N(15)	5 304(13)	6 055(8)	2 041(6)
O(5)	−2 695(10)	5 196(6)	2 213(5)
O(6)	6 432(15)	1 984(10)	3 495(7)
W(2)	1 217.5(6)	1 244.8(3)	2 399.1(2)
O(3)	1 061(11)	482(5)	2 677(4)
O(4)	1 403(8)	2 135(5)	2 147(3)
C(4)	1 633(17)	2 879(8)	2 256(6)
C(21)	1 373(15)	1 894(7)	3 208(6)
N(21)	1 431(13)	2 250(6)	3 616(5)
C(22)	−71(16)	816(8)	1 701(7)
N(22)	−749(14)	611(8)	1 343(6)
C(23)	2 373(18)	828(9)	1 734(7)
N(23)	2 945(17)	584(9)	1 396(7)
C(24)	3 261(16)	1 542(8)	2 639(7)
N(24)	4 227(17)	1 742(8)	2 808(7)
C(25)	−642(16)	1 411(9)	2 640(6)
N(25)	−1 679(15)	1 513(11)	2 743(8)
P(1)	7 261(4)	−470(2)	4 131(2)
C(111)	6 819(14)	−941(7)	4 672(5)
C(112)	5 620(16)	−974(8)	4 868(7)
C(113)	5 306(20)	−1 265(10)	5 319(9)
C(114)	6 210(24)	−1 556(10)	5 581(7)
C(115)	7 411(18)	−1 532(9)	5 397(7)
C(116)	7 725(14)	−1 238(8)	4 938(6)
C(121)	7 881(13)	428(8)	4 413(6)
C(122)	7 857(14)	660(8)	4 969(7)
C(123)	8 340(18)	1 362(10)	5 179(8)
C(124)	8 809(18)	1 846(12)	4 852(11)
C(125)	8 835(17)	1 622(11)	4 307(9)
C(126)	8 419(14)	911(9)	4 083(7)
C(131)	8 450(14)	−878(9)	3 761(6)
C(132)	9 653(17)	−522(10)	3 721(8)
C(133)	10 540(20)	−873(14)	3 449(10)
C(134)	10 230(23)	−1 562(12)	3 235(8)
C(135)	9 064(24)	−1 922(11)	3 264(8)
C(136)	8 155(17)	−1 586(9)	3 520(6)
C(141)	5 891(14)	−507(8)	3 680(6)
C(142)	5 118(17)	−1 143(8)	3 534(8)
C(143)	4 130(20)	−1 190(11)	3 179(9)
C(144)	3 884(19)	−619(14)	2 967(7)
C(145)	4 663(19)	32(11)	3 138(8)
C(146)	5 689(17)	82(9)	3 485(7)
P(2)	2 473(3)	4 648(2)	4 379(1)
C(211)	2 813(12)	5 548(7)	4 758(5)
C(212)	2 843(12)	5 638(7)	5 332(5)
C(213)	3 071(14)	6 304(8)	5 626(6)
C(214)	3 267(14)	6 892(8)	5 351(7)
C(215)	3 258(15)	6 811(8)	4 797(6)
C(216)	3 023(13)	6 150(7)	4 496(6)
C(221)	2 330(13)	4 023(6)	4 845(5)
C(222)	3 396(14)	3 759(7)	4 997(6)
C(223)	3 295(18)	3 348(9)	5 411(8)
C(224)	2 172(22)	3 209(8)	5 642(7)
C(225)	1 067(17)	3 449(8)	5 511(6)
C(226)	1 164(14)	3 867(7)	5 095(6)
C(231)	1 024(11)	4 511(7)	3 979(5)
C(232)	486(13)	3 814(8)	3 745(6)
C(233)	−532(15)	3 698(10)	3 395(7)
C(234)	−1 027(15)	4 241(12)	3 270(7)
C(235)	−542(16)	4 948(10)	3 497(7)
C(236)	513(14)	5 069(9)	3 851(6)
C(241)	3 720(12)	4 470(8)	3 929(5)
C(242)	4 651(13)	5 020(8)	3 810(6)
C(243)	5 512(15)	4 878(12)	3 408(8)
C(244)	5 455(17)	4 183(13)	3 142(7)
C(245)	4 553(15)	3 659(9)	3 257(6)
C(246)	3 686(13)	3 787(8)	3 654(6)
P(3)	3 846(4)	8 125(2)	894(2)
C(311)	3 882(15)	8 615(7)	360(6)
C(312)	2 774(17)	8 793(8)	161(7)
C(313)	2 821(25)	9 080(9)	−329(8)
C(314)	3 890(28)	9 169(11)	−606(10)
C(315)	4 918(23)	8 992(11)	−409(9)
C(316)	4 983(17)	8 737(9)	61(7)
C(321)	3 908(13)	7 206(7)	591(6)
C(322)	3 542(19)	6 984(10)	61(7)
C(323)	3 555(21)	6 269(11)	−153(8)
C(324)	3 833(19)	5 800(10)	132(10)
C(325)	4 192(22)	6 022(10)	634(9)
C(326)	4 241(19)	6 720(10)	885(8)
C(331)	5 128(13)	8 525(9)	1 366(6)
C(332)	5 575(22)	8 190(10)	1 746(9)
C(333)	6 434(27)	8 485(15)	2 115(10)
C(334)	7 031(17)	9 135(16)	2 132(8)
C(335)	6 664(25)	9 486(13)	1 769(10)
C(336)	5 697(22)	9 169(12)	1 398(9)
C(341)	2 392(14)	8 130(8)	1 258(5)
C(342)	2 174(15)	8 790(8)	1 524(6)
C(343)	1 037(17)	8 777(9)	1 786(6)
C(344)	195(15)	8 160(11)	1 795(7)
C(345)	499(16)	7 535(9)	1 522(6)
C(346)	1 549(14)	7 507(8)	1 253(6)
P(4)	1 485(4)	3 040(2)	506(2)
C(411)	222(14)	3 143(8)	950(6)
C(412)	−704(16)	2 579(10)	1 025(8)
C(413)	−1 609(18)	2 659(13)	1 408(10)
C(414)	−1 661(19)	3 329(15)	1 687(9)
C(415)	−796(21)	3 905(12)	1 624(7)
C(416)	171(16)	3 826(9)	1 257(6)
C(421)	1 342(12)	2 122(7)	191(6)
C(422)	1 364(13)	1 606(7)	517(6)
C(423)	1 310(15)	890(8)	286(7)
C(424)	1 226(16)	716(8)	−285(7)
C(425)	1 137(15)	1 209(8)	−595(6)
C(426)	1 255(15)	1 939(8)	−363(6)
C(431)	1 454(18)	3 580(7)	−22(6)
C(432)	342(17)	3 867(8)	−110(6)
C(433)	279(22)	4 236(9)	−542(8)
C(434)	1 262(27)	4 296(10)	−891(9)
C(435)	2 336(23)	4 032(10)	−793(8)
C(436)	2 447(17)	3 661(9)	−365(7)
C(441)	2 965(11)	3 329(8)	872(5)
C(442)	3 336(15)	4 038(8)	1 044(6)
C(443)	4 428(16)	4 269(9)	1 382(7)
C(444)	5 106(15)	3 829(11)	1 532(7)
C(445)	4 773(17)	3 106(10)	1 357(7)
C(446)	3 668(16)	2 854(9)	1 028(7)

Results and Discussion

It has been established previously[4] that when *high* light intensities are used, the photochemistry of $[W(CN)_8]^{3-}$ ion is changed from the simple one-electron photoreduction of the metal centre by solvent [equation (1)] to a more complex pathway leading to highly coloured products. In aqueous

Table 4. Principal bond lengths (Å) and angles (°) for $[PPh_4]_2[W(CN)_5O(OMe)]$

W(1)–O(1)	1.919(9)	W(1)–O(2)	1.701(9)
W(1)–C(11)	2.173(14)	W(1)–C(12)	2.168(14)
W(1)–C(13)	2.136(18)	W(1)–C(14)	2.190(15)
W(1)–C(15)	2.151(17)	O(1)–C(1)	1.395(14)
C(11)–N(11)	1.163(19)	C(12)–N(12)	1.136(19)
C(13)–N(13)	1.147(23)	C(14)–N(14)	1.141(19)
C(15)–N(15)	1.140(22)	W(2)–O(3)	1.700(10)
W(2)–O(4)	1.893(9)	W(2)–C(21)	2.175(14)
W(2)–C(22)	2.167(15)	W(2)–C(23)	2.201(18)
W(2)–C(24)	2.219(16)	W(2)–C(25)	2.145(18)
O(4)–C(4)	1.391(17)	C(21)–N(21)	1.122(18)
C(22)–N(22)	1.121(21)	C(23)–N(23)	1.129(25)
C(24)–N(24)	1.097(23)	C(25)–N(25)	1.183(25)
O(1)–W(1)–O(2)	173.0(4)	O(1)–W(1)–C(11)	90.1(5)
O(2)–W(1)–C(11)	94.4(5)	O(1)–W(1)–C(12)	90.9(5)
O(2)–W(1)–C(12)	95.6(5)	C(11)–W(1)–C(12)	72.1(5)
O(1)–W(1)–C(13)	88.3(5)	C(2)–W(1)–C(13)	91.3(5)
O(1)–W(1)–C(14)	83.5(6)	O(2)–W(1)–C(14)	89.7(5)
C(13)–W(1)–C(14)	70.9(6)	O(1)–W(1)–C(15)	85.6(5)
O(2)–W(1)–C(15)	90.6(5)	C(11)–W(1)–C(15)	72.5(5)
C(14)–W(1)–C(15)	72.7(5)	W(1)–O(1)–C(1)	143.1(8)
W(1)–C(11)–N(11)	179.0(13)	W(1)–C(12)–N(12)	178.4(13)
W(1)–C(13)–N(13)	178.0(13)	W(1)–C(14)–N(14)	176.7(15)
W(1)–C(15)–N(15)	179.4(12)	O(3)–W(2)–O(4)	175.4(4)
O(3)–W(2)–C(21)	91.0(5)	O(4)–W(2)–C(21)	84.4(5)
O(3)–W(2)–C(22)	96.4(5)	O(4)–W(2)–C(22)	87.3(5)
O(4)–W(2)–C(23)	90.4(5)	O(3)–W(2)–C(23)	93.2(6)
C(22)–W(2)–C(23)	73.6(6)	O(3)–W(2)–C(24)	93.0(6)
O(4)–W(2)–C(24)	85.6(5)	C(21)–W(2)–C(24)	72.5(6)
O(3)–W(2)–C(25)	91.1(6)	C(23)–W(2)–C(24)	69.6(6)
C(21)–W(2)–C(25)	71.24(6)	O(4)–W(2)–C(25)	87.5(5)
W(2)–O(4)–C(25)	149.9(9)	C(22)–W(2)–C(25)	72.6(6)
W(2)–C(22)–N(22)	178.1(15)	W(2)–C(21)–N(21)	177.1(14)
W(2)–C(24)–N(24)	171.6(16)	W(2)–C(23)–N(23)	176.9(15)
		W(2)–C(25)–N(25)	176.1(16)

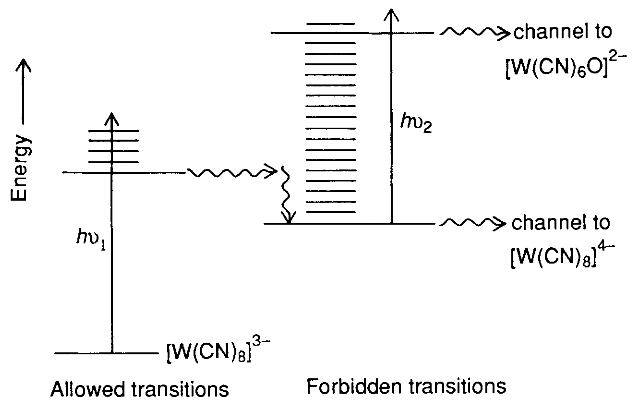


Figure 3. Schematic diagram of two-quantum process leading to tungsten(VI) photoproducts

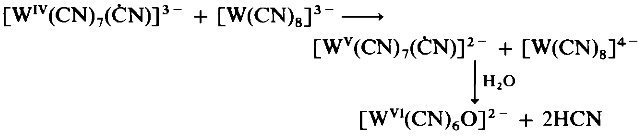
solution a red-purple product ($\lambda_{max.}$ 535 nm) is formed {assigned to $[W^{IV}(CN)_7(O_2)]^{3-}$ ion}[4] while in aqueous methanol this material changes on standing to a deep violet material ($\lambda_{max.}$ 560 nm) {assigned to the dimeric $[(NC)_7WO_2W(CN)_7]^{6-}$ ion}.[4]

The Colourless Products.—We find optical changes identical to those referred to above both in water (but with $\lambda_{max.}$ 537 nm) and aqueous methanol. While the instability towards isolation of the photoproduct ($\lambda_{max.}$ 537 nm) of the intense photolysis of aqueous $[W(CN)_8]^{3-}$ ion precluded its structure determination in the solid state, precipitation of the photolysate by PPh_4Cl yielded the colourless compound (**1**), characterized by *X*-ray diffraction as $[PPh_4]_2[W^{VI}(CN)_6O]{\cdot}H_2O$.

The photoproduction of $[W(CN)_6O]^{2-}$ under high-intensity photolysis is both unexpected and interesting. The $[W(CN)_8]^{3-}$ ion is oxidizing (E^0 0.457 V *vs.* n.h.e.)[9] and its reaction on excitation under normal light intensity is the expected attack on solvent, equation (1). The production of a tungsten(VI) complex requires net *oxidation* of W^V, and, for example, $[W(CN)_8]^{2-}$ has never been recorded except as a gas-phase species following f.a.b. of a glycerol matrix of $K_3[W(CN)_8]$.[10] Noting that complex (**1**) is produced only under high-intensity irradiation, one explanation for this highly endoergonic process involves a two-quantum process involving, as a light-absorbing intermediate, either a long-lived excited state or a short-lived reactive intermediate (Figure 3). This is supported by a very detailed kinetic study of the production of the photoproduct ($\lambda_{max.}$ 537 nm) which will be published elsewhere,[11] which demonstrates (*i*) that in the wavelength range $360 > \lambda_{irr} > 310$ nm, the rate of formation of the product ($\lambda_{max.}$ 537 nm) depends on the *square* of the effective light intensity and (*ii*) at very short wavelengths ($\lambda < 230$ nm) this compound is produced monophotonically in relatively high yield ($\Phi \approx 0.1$).

Two-quantum processes are comparatively rare in inorganic photochemistry, but a number have recently been established, *e.g.* (*a*) the photoaquation of $[Cr(phen)_3]^{3+}$ (phen = 1,10-phenanthroline),[12] (*b*) in luminescence quenching, at high excitation intensities, of a polypyridyl complex of Ru^{II} by a polytungstate anion,[13] and (*c*) the excited-state disproportionation of $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridyl).[14]

An intermediate exhibiting unusual behaviour has been detected on conventional microsecond and 249-nm laser flash photolysis of aqueous $[W(CN)_8]^{3-}$ ion.[15] This has $\lambda_{max.}$ 410 nm and τ (298 K) $\approx$5.4 ms. An extreme lifetime dependence on the presence of added electrolytes led to its assignment to a radical-pair configuration, $\{[W^{IV}(CN)_7(\dot{C}N)^{3-}, M^+\}$ ($M^+ = H^+, Li^+, Na^+, Cs^+, NH_4^+, NEt_4^+$, or Ca^{2+}). Absorption of a second quantum could lead to further charge separation, leading to a higher oxidation state of the metal, concomitant with a ligand-field photosubstitution by solvent (Scheme).



$$[W^{IV}(CN)_7(\dot{C}N)]^{3-} + [W(CN)_8]^{3-} \longrightarrow [W^{V}(CN)_7(\dot{C}N)]^{2-} + [W(CN)_8]^{4-} \xrightarrow{H_2O} [W^{VI}(CN)_6O]^{2-} + 2HCN$$

Scheme.

A simpler alternative intermediate would be doubly excited $[W(CN)_8]^{3-}$ ion, which could disproportionate in electron transfer with a ground-state $[W(CN)_8]^{3-}$ ion [equation (2)].

$$([W(CN)_8]^{3-})^{**} + [W(CN)_8]^{3-} \longrightarrow [W^{VI}(\dot{C}N)_8]^{2-} + [W(CN)_8]^{4-} \quad (2)$$

Nucleophilic substitution of $[W^{VI}(CN)_8]^{2-}$ to give $[W^{VI}(CN)_6(OH)_2]^{2-}$ would be followed by elimination of water to produce $[W(CN)_6O]^{2-}$ as isolated.

The recovery of complex (**2**) on allowing a photolysed solution of $[W(CN)_8]^{3-}$ in aqueous methanol to stand for 48 h reflects the lability of the ligand *trans* to the oxo-group towards nucleophilic substitution by methanol or methoxide ion.

The ions in both complex (**1**) and (**2**) have pentagonal-bipyramidal geometry. In both the equatorial CN^- groups are bent slightly away from the W=O apex (angles O–W–C of 95—99°); this is presumably due to repulsion by the π electrons in the W=O double bond. The geometry parallels those of a number of transition-metal cyano-complexes, *viz.* $[V(CN)_6(NO)]^{4-}$,[16,17]

$[Mo(CN)_7]^{5-}$,[18] $[Mo(CN)_7]^{4-}$,[19] and $[Re(CN)_7]^{4-}$.[20] However, no previous example with W as the central atom has been reported.

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