Inorganica Chimica Acta, 163 (1989) 127–128

New Photo-products in the High-intensity Solution Photolysis of Octacyanotungstate(V) Ion: Definition of a High-energy Photochemical Channel

BARBARA SIEKLUCKA*

Faculty of Chemistry, Jagiellonian University, Karasia 3,
30-060 Krakow (Poland)

NATHANIEL W. ALCOCK, TERENCE J. KEMP,
LASZLO VINCZE

Department of Chemistry, University of Warwick,
Coventry CV4 7AL (U.K.)

and DERK J. STUFKENS

Anorganisch Chemisch Laboratorium, Universiteit van
Amsterdam, Nieuwe Achtergracht 166,
1018 WV Amsterdam (The Netherlands)

(Received April 10, 1989)

Photolysis of $[W(CN)_8]^{3-}$ ion in water [1–3] and non-aqueous solvents [4] normally produces $[W(CN)_8]^{4-}$ in high yield (ϕ = *c.* 0.8 in water [3]) via the photoredox process (in water)

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

One of us (B.S.) has reported previously [5] that under conditions of *high* light intensity, a new pathway emerges, yielding a red–purple solution (λ_{max} 537 nm). Photolysis in water–methanol (1:1 vol./vol.) led to conversion of the 537 nm product to a deep violet material (λ_{max} 560 nm). Both of these diamagnetic photo-products were attributed [5] to dioxygen complexes of W^{IV}.

We now report that, following precipitation procedures with $PPh_4^+Cl^-$, we have isolated from the aqueous photolysate containing the mixture of photo-products, after high-intensity photolysis (focused output of a 200 W Xe/Hg lamp) of a 0.01 mol dm^{-3} solution of $K_3[W(CN)_8]$, the almost colourless (palest pink) W^{VI} product $(PPh_4)_2[WO(CN)_6]\cdot H_2O$ (**1**), and from methanol–water the analogous almost colourless (palest violet) $(PPh_4)_2[WO(CN)_5(OMe)]$ (**2**). (Both complexes gave analytical and spectral data consistent with their structures. Selected IR data for **1** (KBr): ν(CN) 2206, 2159, 2143; ν(W=O) 963 cm^{-1} and for **2** (KBr): ν(CH) 2920, 2825; ν(CN) 2206, 2164; ν(W=O) 933 cm^{-1}.)

The structures of both of these complexes (after recrystallisation from methanol) have been obtained by X-ray diffraction, both anions being pentagonal bipyramidal (Fig. 1(a) and (b)) with all equatorial positions occupied by CN^- ligands. (Crystal data for **1**: triclinic, $P\bar{1}$, with a = 10.247(2), b = 14.510(3), c = 16.394(3) Å, α = 103.19(2), β = 90.78(1), γ = 92.21(2)°, U = 2307.8(7) Å, Z = 2, R = 0.028 for 6785 unique, observed reflections ($I/\sigma(I) > 3.0$). Crystal data for **2**: triclinic, $P\bar{1}$, a = 10.713(3), b = 19.208(5), c = 24.787(6) Å, α = 99.17(2), β = 90.64(2), γ = 99.40(2)°, U = 4964(2), Z = 4, R = 0.051 for 6865 unique observed reflections ($I/\sigma(I) > 2$).) Their geometry conforms to that of such anions as $[V(CN)_6(NO)]^{4-}$ [6, 7], $[Mo(CN)_7]^{5-}$ [8], $[Mo(CN)_7]^{4-}$ [9] and $[Re(CN)_7]^{4-}$ [10].

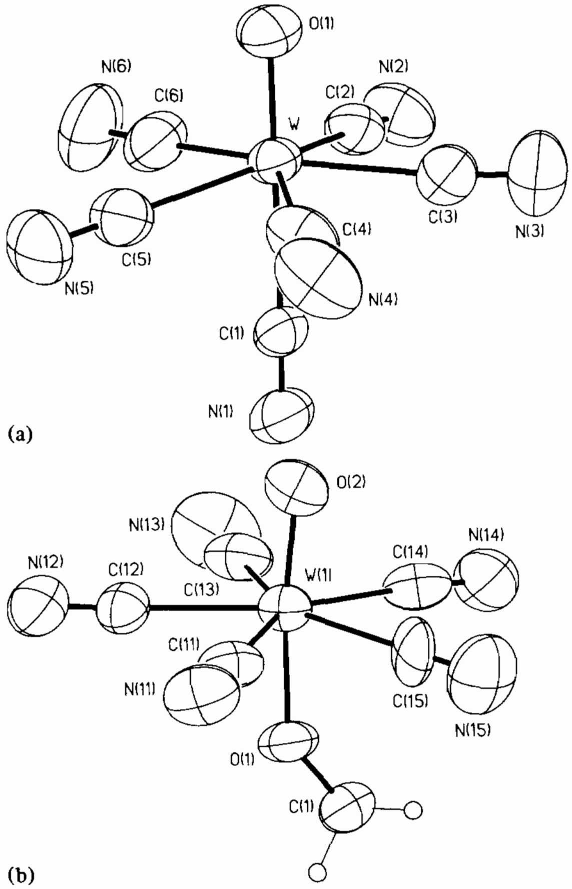

Fig. 1. (a) View of the anion $[WO(CN)_6]^{2-}$ in crystalline $[PPh_4]_2[WO(CN)_6]$. H_2O isolated from the high-intensity photolysate of $[W(CN)_8]^{3-}$ in water. Selected average distances and angles are: W=O 1.691(3), W–C_{ax} 2.277(3), W–C_{eq} 2.150(5) Å (mean), O(1)–W–C_{ax} 177.1°. (b) View of one of the two independent anions $[WO(CN)_5(OMe)]^{2-}$ in crystalline $[PPh_4]_2[WO(CN)_5(OMe)]$ isolated from the high-intensity photolysate of $[W(CN)_8]^{3-}$ in water–methanol (1:1). Selected average distances and angles are: W=O(2) 1.700(8), W–O(1) 1.906(8), W–C_{eq} 2.172(12) Å (mean), W–O(1)–C(1) 143.1(8) and 149.9(8)°.

The chief mechanistic interest lies in the unexpected production of W^{VI}: this contrasts with the

---

*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

normal route, eqn. (1) and implies either disproportionation of a W^{V} intermediate or a high-energy route. Detailed quantum yield investigation of the formation of the (still uncharacterised) 537 nm photo-product indicates that this is formed in a (probably *sequential*) biphotonic process [11], with a formation rate dependent on the *square* of the incident light intensity, when 360 nm $> \lambda >$ 310 nm. (The species absorbing the second photon can be either a long-lived excited state or a reactive intermediate.) Since production of the crystalline W^{VI} species described occurs in parallel with those of the 537 and 560 nm photo-products, we attribute formation of these unusual W^{VI} photo-products also to a biphotonic route.

Such two-quantum processes, while common in organic photochemistry, are rare in solution inorganic photochemistry, recent instances being (i) the photoaquation of $[Cr(phen)_3]^{3+}$ (phen = 1,10-phenanthroline) [12]; (ii) in luminescence quenching, at high excitation intensities, of a polypyridyl complex of Ru^{II} by a polytungstate anion [13]; (iii) the excited state disproportionation of $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridyl) [14].

References

1 V. Carassiti and V. Balzani, *Ann. Chim. (Rome), 51* (1961) 518; V. Balzani and V. Carassiti, *Ann. Chim. (Rome), 51* (1961) 533.
2 A. Samotus, *Rocz. Chem., 47* (1973) 265.
3 B. Sieklucka, A. Kanas and A. Samotus, *Transition Met. Chem., 7* (1982) 131.
4 T. J. Kemp, M. A. Shand and D. Rehorek, *J. Chem. Soc., Dalton Trans.*, (1988) 285.
5 B. Sieklucka, A. Samotus, S. Sostero and O. Traverso, *Inorg. Chim. Acta, 86* (1984) L51.
6 M. G. B. Drew and C. F. Pygall, *Acta Crystallogr., Sect. B, 33* (1977) 2838.
7 S. Jagner and E. Ljungström, *Acta Crystallogr., Sect. B, 34* (1978) 653.
8 M. G. B. Drew, P. C. H. Mitchell and C. F. Pygall, *J. Chem. Soc., Dalton Trans.*, (1977) 1071.
9 M. B. Hursthouse, K. M. A. Malik, A. M. Soares, J. F. Gibson and W. P. Griffith, *Inorg. Chim. Acta, 45* (1980) L81.
10 J. M. Manoli, C. Potvin, J. M. Bregeault and W. P. Griffith, *J. Chem. Soc., Dalton Trans.*, (1980) 192.
11 T. J. Kemp and L. Vincze, to be published.
12 B. Van Vlieberge and G. Ferraudi, *Inorg. Chem., 27* (1988) 1386.
13 R. Ballardini, M. T. Gandolfi and V. Balzani, *J. Phys. Chem., 92* (1988) 56.
14 G. Ferraudi and G. A. Arguello, *Inorg. Chim. Acta, 144* (1988) 53, and refs. therein.