

A Photochemical Route to Tungsten(IV) Dioxygen-Cyanocomplexes

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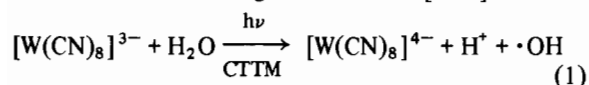
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High-intensity photolysis of $[\text{W}(\text{CN})_8]^{3-}$ in aqueous or aqueous–methanol solutions gives the novel dioxygen complexes $[(\text{CN})_7\text{WO}_2]^{3-}$ and $[(\text{CN})_7\text{WO}_2\text{W}(\text{CN})_7]^{6-}$.

The formation of such products, spin trapping experiments and spectroscopic results provide evidence for the operation of a free radical mechanism involving splitting of water in the photolysis of $[\text{W}(\text{CN})_8]^{3-}$.

Irradiation of aqueous solutions of the octacyanotungstate(V) ion in the CTTM band gives $[\text{W}(\text{CN})_8]^{4-}$ and $\cdot\text{OH}$ radicals during the initial act [1–5]:



This photoredox process is apparently not associated with the formation of any other relatively stable tungsten species, except in low pH solutions (pH \leq 2) [3]. However, when aqueous solutions of $[\text{W}(\text{CN})_8]^{3-}$ are photolyzed with high intensity light (200–500 W) two new dioxygen complexes of tungsten (IV), $[(\text{CN})_7\text{WO}_2]^{3-}$ and $[(\text{CN})_7\text{WO}_2\text{W}(\text{CN})_7]^{6-}$ are obtained.

In this paper the preparation and spectroscopic properties of these new species are reported.

Experimental

Materials

$\text{K}_3[\text{W}(\text{CN})_8] \cdot 1.5\text{H}_2\text{O}$ was prepared as previously described [2].

Conventional buffer solutions of pH 1–13 were made according to the Bates method [6]. The pH's of each reaction mixture were measured by means of an N-512 pH-meter. All solvents used were of spectroscopic grade. 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) was a commercial sample used as received.

General Irradiation Procedures

Irradiations were conducted using a high pressure mercury lamp HBO 200 and/or 500 W OSRMAN lamp equipped with a WG-305 cut-off filter.

Freshly prepared 0.01 M solutions of $\text{K}_3[\text{W}(\text{CN})_8]$ were photolyzed in a spectrophotometric 1 cm quartz cell. The photolysis was carried out at room temperature and performed under oxygen-free conditions. Electronic spectra were recorded periodically with a Cary 219 and/or a Perkin-Elmer 323 spectrometer. Solutions for Raman studies were transferred into the appropriate cell within an inert atmosphere glove box. The bands of CH_3OH were used as internal standard. Raman spectra were recorded with a Cary 82 spectrometer using the 514.5 nm excitation-line. The ESR experiments were carried out with a Bruker ER 200 spectrometer.

Photochemical Preparation of $[(\text{CN})_7\text{WO}_2]^{3-}$, (I)

$\text{K}_3[\text{W}(\text{CN})_8] \cdot 1.5\text{H}_2\text{O}$ (0.268 g) in 50 ml of water–methanol (1:1) was bubbled with nitrogen for 20 min in a Vycor reaction tube. The reaction mixture was then degassed by alternately freezing and thawing to ensure removal of oxygen. The reaction vessel was then placed in a Pyrex jacket and irradiation was begun. During irradiation, the solution gradually turned from colourless to red and remained clear. The photoreaction progress was followed by monitoring the increase of the W–O₂ CT band at 535 nm of complex I and the growth of its Raman spectrum $\nu(\text{O}_2)$ peak. The electronic and Raman spectral data show that the photolyzed $[\text{W}(\text{CN})_8]^{3-}$ had been converted to I ($\lambda_{\text{max}} = 535 \text{ nm}$; $\nu(\text{O}_2)$ at 1000 and 1345 cm^{-1}). This compound is not isolated; it does not crystallize upon cooling and removal of the solvent under vacuum causes decomposition.

Formation and Isolation of $\text{Cd}_3[(\text{CN})_7\text{W}_2\text{O}_2(\text{CN})_7] \cdot 12\text{H}_2\text{O}$, (II)

Solutions of I were prepared by photolysis of $[\text{W}(\text{CN})_8]^{3-}$ in water–methanol as described before. While standing in the dark at room temperature the solutions of I turned deep violet. Addition of CdCl_2 to these violet solutions produced a precipitate of $\text{Cd}_2[\text{W}(\text{CN})_8] \cdot 6\text{H}_2\text{O}$ which was removed by filtration. A CdCl_2 addition to the filtered solution precipitated dark blue salt which was removed by filtration and washed with water–methanol (1:1). *Anal.* Calcd. for $\text{Cd}_3[\text{W}_2\text{O}_2(\text{CN})_{14}] \cdot 12\text{H}_2\text{O}$: Cd, 25.6; W, 27.89; C, 12.75; N, 14.94; H, 1.83%. Found: Cd, 26.1; W, 27.28; C, 12.93; N, 14.95; H, 1.77%. Mol. Wt. 1305. A thermal decomposition (160 °C) of Cd salt caused a weight loss corresponding to 17.2% per dinuclear complex (calcd. loss for $(12\text{H}_2\text{O} + \frac{1}{2}\text{O}_2)$, 17.6%).

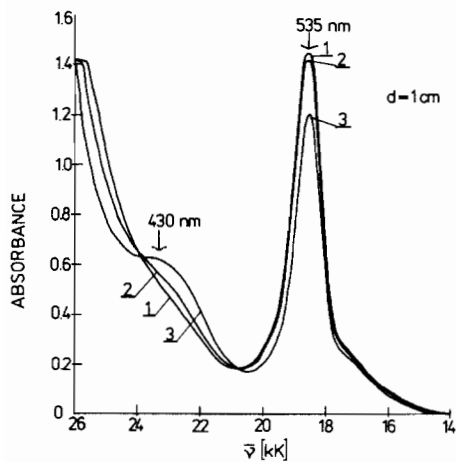


Fig. 1. Time-decay absorption spectrum of irradiated ($t_{\text{irr}} = 5\text{ s}$) 0.01 M $[\text{W}(\text{CN})_8]^{3-}$ solution in H_2O ; 1 = 15 s, 2 = 6 min, 3 = 24 h.

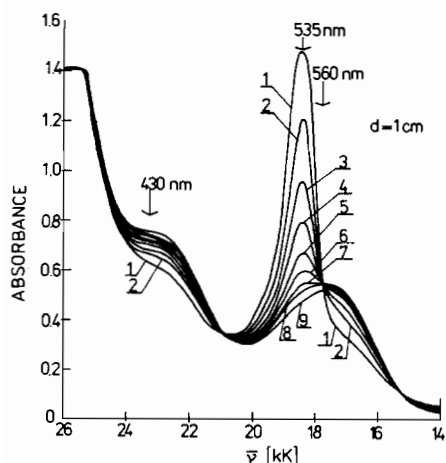


Fig. 2. Time-decay absorption spectrum of irradiated ($t_{\text{irr}} = 5\text{ s}$) 0.01 M $[\text{W}(\text{CN})_8]^{3-}$ solution at $\text{pH} = 9.35$; 1 = 15 s, 2 = 2 min, 3 = 4 min, 4 = 9 min, 5 = 12 min, 6 = 16 min, 7 = 21 min, 8 = 21 min, 9 = 88 min.

Electronic spectrum (saturated KCl solution): 560 nm ($\epsilon = 1.00 \times 10^3$), 380 nm ($\epsilon = 8.27 \times 10^2$), 250 nm ($\epsilon = 3.86 \times 10^4$).

IR spectrum (KBr): 395 m, 460 m, 1405 w, 1610 vs, 2140 vs broad, 3400–3600 s broad.

Raman spectrum (solid): 425 w, 915–925 s, 1400 vs, 2165 m, 2330–2340 m.

Results and Discussion

Irradiation of $[\text{W}(\text{CN})_8]^{3-}$ solutions induced a rapid initial change from colorless to red. The electronic absorption spectral changes which occur during photolysis ($\lambda > 305\text{ nm}$) of a degassed $[\text{W}(\text{CN})_8]^{3-}$ solution are strongly pH- and solvent-dependent.

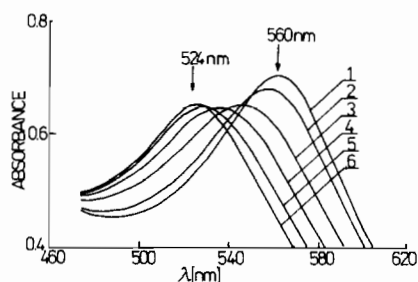


Fig. 3. Changes in the absorption spectrum of complex II solution after acidification with HClO_4 , 1 = 2 min, 2 = 9 min, 3 = 30 min, 4 = 56 min, 5 = 97 min, 6 = 148 min.

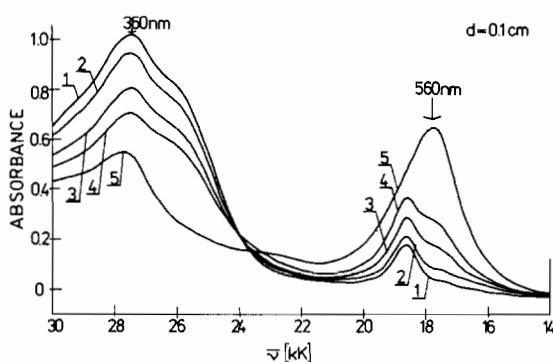


Fig. 4. Absorption spectra of irradiated ($t_{\text{irr}} = 30\text{ s}$) 0.01 M $[\text{W}(\text{CN})_8]^{3-}$ solution in $\text{H}_2\text{O}-\text{CH}_3\text{OH}$ (1:1) mixture, illustrating the formation of violet complex II; 1 = 1.5 min, 2 = 16 min, 3 = 61 min, 4 = 114 min, 5 = 72 h.

In general, as the irradiation proceeds a new band appears at 535 nm (Fig. 1). The red product disappears slowly by thermal reaction together with increasing absorbance around 430 nm, characteristic for $[\text{W}(\text{CN})_8]^{4-}$ ion (Fig. 1). Under alkaline conditions in the dark the red species I partially turned to the violet II having the absorption peak at 560 nm (Fig. 2). The acidification of the violet solution gives the spectral variations reported in Fig. 3. The observed spectral variations are due to the formation of $[\text{W}(\text{CN})_7(\text{H}_2\text{O})]^{3-}$ ($\lambda_{\text{max}} = 520\text{ nm}$) [7] and of the complex I ($\lambda_{\text{max}} = 535\text{ nm}$). The formation of complex II is facilitated by using less polar solvents, as indicated by spectral changes observed for irradiated water alcoholic (1:1) and water–dioxan solutions (Fig. 4).

Raman Experiments

Photogeneration of the red I and the violet II complexes has found strong support in the Raman experiments. A solution of $[\text{W}(\text{CN})_8]^{3-}$ was irradiated to generate the complex I. Two very intense bands (A) at 1000 and 1345 cm^{-1} were observed (Fig. 5). As shown in Fig. 5 these bands become weaker (B) and two new band (C) finally appeared at 935 and 1400 cm^{-1} , when the solution turned violet (com-

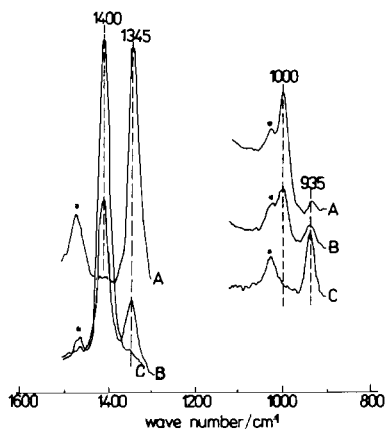


Fig. 5. Raman spectra of irradiated 0.01 M $[\text{W}(\text{CN})_8]^{3-}$ solution in $\text{H}_2\text{O}-\text{CH}_3\text{OH}$ (1:1) mixture, illustrating the transformation of complex I to complex II.

plex II). Solid cadmium salts of a violet species, which we postulate to be 2:1 $\text{W}-\text{O}_2$ complex (II), also exhibited intense bands at 920 and 1400 cm^{-1} . The bands at 1345 and 1400 cm^{-1} are due to O_2 stretching vibrations in mononuclear I and binuclear II complexes respectively. A comparison of the 1345 and 1400 cm^{-1} frequencies with those observed for neutral O_2 [$\nu(^3\text{O}_2) = 1554.7\text{ cm}^{-1}$, $\nu(^1\text{O}_2) = 1483.5\text{ cm}^{-1}$] and O_2 in ionic forms ($\nu(\text{O}_2^-)$, 1145 cm^{-1} ; $\nu(\text{O}_2^{2-})$, 842 cm^{-1}], as well as in several dioxygen metal complexes [8–15], support the above assignments.

The O_2 stretching vibrations in I and II provide valuable information about the nature of the intensive low-energy electronic spectra of these complexes. Laser excitation of the complexes in the 500–600 nm region cause resonance enhancement [16] of $\nu(\text{O}_2)$ at 1345 (I) and 1400 cm^{-1} (II). This result suggests that the electronic bands at 535 and 560 nm are due to the $\text{W}-\text{O}_2$ CTML transitions [11, 13, 17, 18] in the dioxygen complexes I and II respectively.

ESR Experiments

Irradiation of $[\text{W}(\text{CN})_8]^{3-}$ solutions (0.01 M) in an ESR cavity causes a gradual disappearance of the signal at $g_{\text{av}} = 1.972$, characteristic of $[\text{W}(\text{CN})_8]^{3-}$ [19, 20] and the appearance of a new weak signal at $g_{\text{av}} = 1.943$ (Fig. 6). The presence of two hyperfine lines and the value of $A_{1\text{iso}} \sim 56 \times 10^{-4}\text{ cm}^{-1}$, comparable with the original hyperfine splitting $A_{1\text{iso}} \sim 54 \times 10^{-4}\text{ cm}^{-1}$ for $[\text{W}(\text{CN})_8]^{3-}$ [19, 20], suggests that the paramagnetic species formed could be the $[\text{W}^{\text{V}}(\text{CN})_7(\text{H}_2\text{O})]^{2-}$ complex. A gradual disappearance of the signal at $g_{\text{av}} = 1.943$ was observed during prolonged photolysis.

Spin Trapping Experiments

Photolysis of degassed aqueous solutions of $[\text{W}(\text{CN})_8]^{3-}$ (0.01 M) in the presence of DMPO

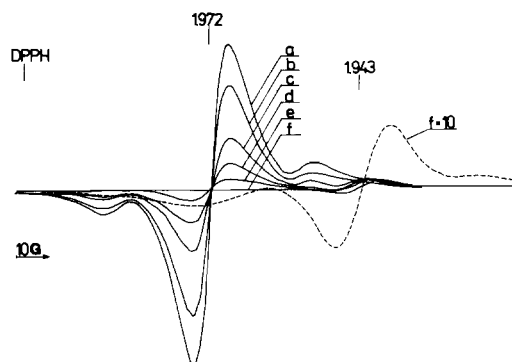


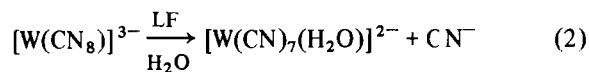
Fig. 6. EPR isotropic solution spectra at room temperature of irradiated 0.01 M $[\text{W}(\text{CN})_8]^{3-}$ solution in H_2O , illustrating the effect of irradiation time; a = unirradiated; b, c, d, e, f = irradiated 30, 60, 90, 120 and 150 s, respectively.

(10^{-1} M) as a spin trap generates an ESR signal ($g = 2.006$) with a 1:1:2:1 quartet pattern ($a^{\text{N}} = a^{\text{H}} = 15.3\text{ G}$) typical of $\text{DMPO}\cdot\text{OH}$ adducts [21].

The formation of the DMPO adduct is a strong indication that $\cdot\text{OH}$ radicals are involved in the system and confirm eqn. 1. Analysis of the electronic and Raman spectra of the irradiated solutions containing DMPO shows the absence of spectral signals associated with the formation of I and II complexes. This can be explained by inhibition of the radical rearrangements by the trapping of the $\cdot\text{OH}$ generated in the process.

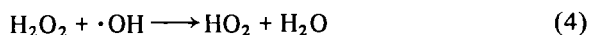
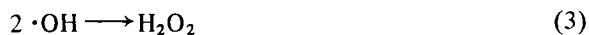
Mechanism Considerations

All the experimental results support the photo-induced formation of the tungsten–dioxygen complexes. Upon irradiation in the 355 nm CTTM transition, aqueous $[\text{W}(\text{CN})_8]^{3-}$ underwent a redox reaction, where $[\text{W}(\text{CN})_8]^{4-}$ and $\cdot\text{OH}$ radicals were formed (eqn. 1). The spin trapping experiments provide evidence of the $\cdot\text{OH}$ formation in the photoredox path. An excited LF state, populated by a radiation-free transition from an initially excited CTTM state [22], can also be a reactive state leading to $[\text{W}(\text{CN})_7(\text{H}_2\text{O})]^{2-}$ and CN^- ions (eqn. 2):

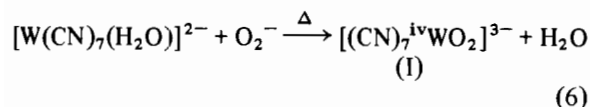


The ESR spectral profile of photoreaction supports the formation of $[\text{W}(\text{CN})_7(\text{H}_2\text{O})]^{2-}$.

The $\cdot\text{OH}$ radicals typically [23] give rise to products derived from disproportionation and from atom abstraction with formation of superoxo ions O_2^- (eqn. 3–5):



The initial photoproduct of substitutional pathway (eqn. 2), $[\text{W}(\text{CN})_7(\text{H}_2\text{O})]^{2-}$, may undergo ligand-substitution reactions by O_2^- with an electron transfer from O_2^- to W^{V} , forming the monomeric dioxygen-heptacyanotungstate (IV):

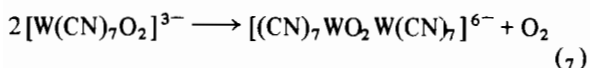


The feasibility of this latter reaction is demonstrated by these experimental results:

i) at the high DMPO concentrations where the trapping of $\cdot\text{OH}$ radicals predominates, no formation of I is observed. The superoxo ions O_2^- cannot be formed when most of the $\cdot\text{OH}$ is trapped.

ii) the formation of complex I is enhanced in neutral and alkaline solutions according to the conjugate-base pathway of HO_2 deprotonation [23].

The O—O stretching frequencies in I and II complexes can be observed simultaneously in solution equilibria. Attempts to isolate the labile I complex from the equilibrium mixture under the above conditions only produced complex II (eqn. 7).



Spectroscopic and crystal structure analyses of complex II are in progress in order to study in detail the overcrowding that is presumed to be the cause of the instability of complex I.

Acknowledgements

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