

# New cyano complex of W(V), $(\text{AsPh}_4)[\text{W}(\text{bpy})(\text{CN})_6]$ : reversible redox system $\text{W}(\text{bpy})(\text{CN})_6^-/\text{W}(\text{bpy})(\text{CN})_6^{2-}$

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(Received July 27, 1992; revised October 22, 1992)

## Abstract

The preparation and spectroscopic characterization of the new cyano complex of W(V),  $(\text{AsPh}_4)[\text{W}(\text{bpy})(\text{CN})_6]$ , is reported. While the light yellow crystalline salt is thermally stable in the solid state and in aqueous solution, in light it undergoes photoreduction to the W(IV) analogue with the initial quantum yield  $\Phi_{365}^0 = 0.17$  in  $\text{H}_2\text{O}$ . The electronic absorption spectrum in the visible part shows ligand-to-metal charge-transfer (LMCT) bands which are solvent dependent. Linear correlations between  $\nu_{\text{max}}$  versus Reichardt  $E_{\text{T}}$  parameter were found. The ESR spectrum at 77 K shows characteristic  $g$  tensors with  $g_1 = 1.9352$ ,  $g_2 = 1.9523$  and  $g_3 = 1.9726$  ( $g_{\text{av}} = 1.9486$  at 293 K). Cyclic voltammetry measurements indicate a reversible one-electron, reduction leading to  $\text{W}(\text{bpy})(\text{CN})_6^{2-}$  with formal redox potential  $E^0 = 0.845$  V (in 0.1 M aqueous KCl), dependent on the nature of the solvent. A new synthetic route to  $(\text{AsPh}_4)_2[\text{W}(\text{bpy})(\text{CN})_6] \cdot 5\text{H}_2\text{O}$  is also presented.

## Introduction

For many years, there has been great interest in polypyridyl and mixed cyano-polypyridyl complexes of transition metals, especially those which form redox pairs [1]. The redox pairs of Fe(II,III), Ru(II,III), Os(II,III) and others have been utilized in many redox systems, as electron relay species and in photochemical systems for conversion of solar energy [2].

Previously we reported the syntheses and properties of  $\text{W}(\text{bpy})(\text{CN})_6^{2-}$  ion salts [3]. The redox potential of the reversible couple and the stability of its W(V) analogue are unknown. In this paper the syntheses and properties of  $\text{W}(\text{bpy})(\text{CN})_6^-$  ion salts are presented. Most attention has been paid to the spectroscopic and redox properties of this new complex, which seems to be comparable with the other cyano-bpy systems.

## Experimental

### Analytical methods

Carbon, nitrogen, hydrogen and tungsten were determined as described earlier [4]. Water was determined by isothermal dehydration *in vacuo* over  $\text{P}_4\text{O}_{10}$ .

### Preparations

All synthetic work was performed under red light.

The initial compound,  $(\text{bpyH})_3(\text{H}_3\text{O})[\text{W}(\text{CN})_8] \cdot \text{H}_2\text{O}$  was synthesized as described earlier [4]. All other reagents were of analytical grade (Aldrich) and used as supplied.

### *Bis(tetraphenylarsonium)(2,2'-bipyridyl)hexacyano-tungstate(IV) pentahydrate, $(\text{AsPh}_4)_2[\text{W}(\text{bpy})(\text{CN})_6] \cdot 5\text{H}_2\text{O}$*

4.0 g (3 mmol) of  $(\text{bpyH})_3(\text{H}_3\text{O})[\text{W}(\text{CN})_8] \cdot \text{H}_2\text{O}$  dissolved in 30 cm<sup>3</sup> of hot anhydrous glycerol were heated up to 150 °C. When the reaction mixture reached an intense blue colour the solution was poured into cold  $\text{H}_2\text{O}$  (c. 150 cm<sup>3</sup>) and a saturated solution of  $\text{CdCl}_2$  was then added to precipitate the reaction products. The precipitate was filtered off, washed with  $\text{H}_2\text{O}$  (up to a negative reaction of  $\text{Cl}^-$  with  $\text{AgNO}_3$ ) and then treated with excess of 1 M NaOH. To the blue-violet solution thus obtained an excess (c. 0.5 g) of  $\text{AsPh}_4\text{Cl}$  in MeOH was added. The mixture was allowed to stand overnight and the resulting dark violet crystals were filtered off and washed with  $\text{H}_2\text{O}$ . The salt was recrystallized three times from  $\text{H}_2\text{O}$ –MeOH (1:2 vol./vol.) solution. Yield c. 50%. *Anal.* Found: C, 56.7; N, 8.4; H, 4.4; W, 13.5,  $\text{H}_2\text{O}$ , 6.6. *Calc.*: C, 56.8; N, 8.3; H, 4.3; W, 13.6,  $\text{H}_2\text{O}$ , 6.7%.

*Tetraphenylarsonium(2,2'-bipyridyl)hexacyano tungstate(V), (AsPh<sub>4</sub>)[W(bpy)(CN)<sub>6</sub>]*

To 0.17 g (0.126 mmol) of (AsPh<sub>4</sub>)<sub>2</sub>[W(bpy)(CN)<sub>6</sub>]·5H<sub>2</sub>O in 3 cm<sup>3</sup> of MeCN, an equivalent amount of H<sub>2</sub>O was added. The resulting solution was acidified with 0.5 cm<sup>3</sup> of 0.2 M HNO<sub>3</sub> and oxidized with 0.1 M KMnO<sub>4</sub>. Then the solution was diluted four times with H<sub>2</sub>O and allowed to stand for one day. The resulting yellow crystals were filtered off, washed three times with H<sub>2</sub>O and recrystallized three times from a MeCN–H<sub>2</sub>O mixture (1:1 vol./vol.). Yield *c.* 70%. *Anal.* Found: C, 54.4; N, 12.8; H, 3.6; W, 20.8. Calc.: C, 54.6; N, 12.7; H, 3.2; W, 20.9%.

The tetraphenylarsonium cation in (AsPh<sub>4</sub>)-[W(bpy)(CN)<sub>6</sub>] can be easily replaced by other cations using MClO<sub>4</sub> solution (M=H<sup>+</sup> or alkali metals) or by passing through a cation exchange column (in H<sup>+</sup> form).

*Physical measurements*

IR absorption spectra in nujoll mulls or in KBr pellets were recorded on a Brüker IFS 48 spectrometer. Electronic absorption spectra were measured with an M-40 spectrophotometer (Carl Zeiss, Jena). ESR spectra were recorded in MeOH with an SE/X-25 spectrometer using dp<sub>pp</sub> (dp<sub>pp</sub> = diphenylpicrylhydrazyl) as a standard. Cyclic voltammetry measurements\* were performed with an Ammel model 552 potentiostat equipped with an Ammel model 568 programmer and Ammel 560/A interface using a three-electrode setup in 0.1 M KCl (H<sub>2</sub>O solutions) or in 0.1 M (Bu<sub>4</sub>N)PF<sub>6</sub> ((Bu<sub>4</sub>N)PF<sub>6</sub> = tetrabutylammonium hexafluorophosphate) for organic solvents. Pt working and counter electrodes and an Ag/AgCl reference electrode were used with sweep rates in the range 0.01–0.5 V s<sup>-1</sup>.

Steady-state photolyses were performed in a 1 cm quartz cell with the focused output of an XBO 150 lamp equipped with a 10 cm path length quartz cell filled with H<sub>2</sub>O for cutting off IR radiation and filtered to isolate the 365 nm line (UV SIF 365 nm interference filter, Carl Zeiss, Jena) of 3.15 × 10<sup>15</sup> quanta s<sup>-1</sup>. The photoreduction of W(CN)<sub>8</sub><sup>3-</sup> in aqueous acidic solutions ( $\Phi=0.81$ ,  $\lambda_{ir}=365$  nm) was used as the actinometer [5]. The solutions of (AsPh<sub>4</sub>)[W(bpy)(CN)<sub>6</sub>] (*c* = 6.0 × 10<sup>-4</sup> M) were deaerated (Ar purged) prior to use. The progress of photoreaction was followed spectrophotometrically at 565 nm ( $\lambda_{max}$  of the metal-to-ligand charge-transfer (MLCT) band of (AsPh<sub>4</sub>)<sub>2</sub>-[W(bpy)(CN)<sub>6</sub>],  $\epsilon_{max}=4.900$  [3]). Quantum yields of formation of W(bpy)(CN)<sub>6</sub><sup>2-</sup> were corrected for the partial transmittance of substrate [6] (up to 15% of conversion). All measurements were performed at room temperature (*c.* 20 ± 2 °C).

\*Measurements were performed in the Department of Chemistry, University of Ferrara, Ferrara, Italy.

**Results and discussion**

*Synthesis and characterization*

Oxidation of (AsPh<sub>4</sub>)<sub>2</sub>[W(bpy)(CN)<sub>6</sub>]·5H<sub>2</sub>O by KMnO<sub>4</sub> in mixed solvent (H<sub>2</sub>O–MeCN) acidic solution gives (AsPh<sub>4</sub>)[W(bpy)(CN)<sub>6</sub>]. The resulting salt is light sensitive as a solid and in solution but in the dark (or in diffuse light) it remains unaltered in air for long periods. It is well soluble in polar organic solvents and sparingly in water.

The synthetic method used previously to obtain (AsPh<sub>4</sub>)<sub>2</sub>[W(bpy)(CN)<sub>6</sub>]·5H<sub>2</sub>O gives the product with a yield not higher than 20% (see ref. 15). In this paper a modified method was used, involving the thermal decomposition of (bpyH)<sub>3</sub>(H<sub>3</sub>O)[W(CN)<sub>8</sub>]·H<sub>2</sub>O in glycerol. The high boiling point and good solubility in water enable the product to be obtained with a yield of *c.* 50%.

*IR spectra*

Data for the prominent bands of (AsPh<sub>4</sub>)[W(bpy)(CN)<sub>6</sub>] (A) that can be rather unambiguously assigned are summarized in Table 1. For comparison, the bands for (AsPh<sub>4</sub>)<sub>2</sub>[W(bpy)(CN)<sub>6</sub>]·5H<sub>2</sub>O (B) are also included. The complex show weak bands at 2118 and 2163 cm<sup>-1</sup> corresponding to C≡N stretching modes which are much weaker than that of the W(IV) analogue and lie almost at the same position as for octacyanotungstate(V) salts [7, 8]. In both salts (A and B) the bands of bpy are diminished in intensity in comparison with the free bpy, without significant change in the band positions [3, 9]. There are no bands in the region typical for water molecules confirming that the salt is anhydrous.

*ESR spectra*

The ESR spectrum in methanol (Fig. 1) at room temperature shows symmetrical signal characteristic for

TABLE 1. Selected IR<sup>a</sup> frequencies for (AsPh<sub>4</sub>)[W(bpy)(CN)<sub>6</sub>] (A) and (AsPh<sub>4</sub>)<sub>2</sub>[W(bpy)(CN)<sub>6</sub>]·5H<sub>2</sub>O (B) salts

Complex	Some bands (in cm <sup>-1</sup> ) characteristic for		
	CN	cation	cation and bpy
A	2163vw 2118vw	1004m 472s	1610m, 1478w, 1448vs, 1322m, 1087s, 783vs, 758vs, 698vs,
B	2135w 2129m 2125m 2118vs 2112vs	1003m 470vs	1610v, 1480s, 1440vs, 1320vw, 1088m, 777s, 755vs, 698s

<sup>a</sup>The abbreviations v, s, m, w, denote very, strong, medium and weak.

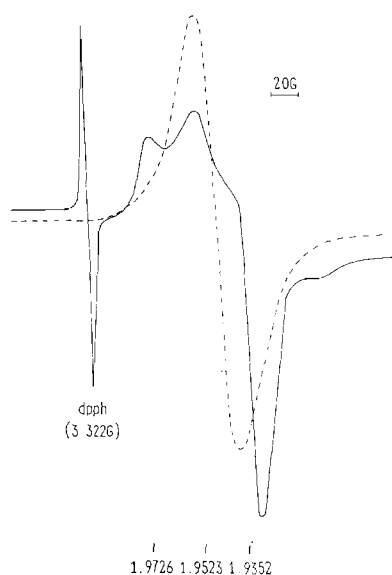


Fig. 1. ESR spectra of  $(\text{AsPh}_4)[\text{W}(\text{bpy})(\text{CN})_6]$  in MeOH solution at 77 (—) and 293 (---) K.

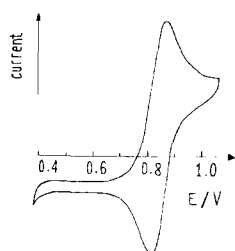


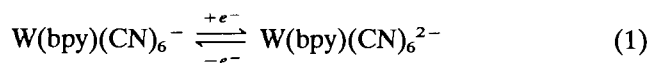
Fig. 2. Cyclic voltammogram of  $1 \times 10^{-4}$  M solution of **B** in 0.1 M KCl ( $\text{H}_2\text{O}$ ) vs. silver chloride electrode; scan speed  $200 \text{ mV s}^{-1}$ , Pt working electrode.

$d^1$ -W complexes. In glassy methanol (77 K) however, the signal loses its symmetry and  $g_1$ ,  $g_2$  and  $g_3$  can be calculated. The values of  $g$  tensors;  $g_1=1.9352$ ,  $g_2=1.9523$  and  $g_3=1.9726$  with  $g_{\text{av}}=1.9486$  and  $A(^{183}\text{W})=32.3 \text{ G}$  are smaller than that for the  $\text{W}(\text{CN})_8^{3-}$  ion ( $g_{\parallel}=1.980$ ,  $g_{\perp}=1.965$  with  $g_{\text{av}}=1.9705$  [10]) but are similar to those of substituted octacyanides such as  $\text{W}(\text{CN})_7(\text{H}_2\text{O})^{2-}$  ( $g_{\text{av}}=1.9482$ ) [11]. The presence of  $g_1$ - $g_3$  tensors suggests that the complex is fully anisotropic, without axial symmetry. Probably in this system, similar to  $(\text{AsPh}_4)[\text{WO}(\text{bpy})(\text{CN})_3] \cdot 2\text{H}_2\text{O} \cdot 0.5 \text{ bpy}$  [12], the bpy ligand is distorted and the pyridine rings are not equivalent. This supposition is supported by the results obtained for the 1,10-phenanthroline (phen) analogue [13] for which  $g_{\perp}$  and  $g_{\parallel}$  can be calculated (being consistent with the fact that the phen ligand is more rigid and cannot be distorted).

#### Cyclic voltammetry

Cyclic voltammetry measurements, performed in aqueous solution in the range  $-0.5$  to  $1.0 \text{ V}$ , indicate (Fig. 2) that only one wave, typical for a reversible

one-electron transfer appears (eqn. (1))



with formal redox potential  $E^0=0.845 \text{ V}$  and  $\alpha E=70 \text{ mV}$  ( $0.1 \text{ M KCl}$ ). The redox potential is solvent dependent and decreases in the order  $\text{H}_2\text{O} > \text{MeOH}$  ( $E^0=0.751 \text{ V}$ )  $> \text{Me}_2\text{CO}$  ( $E^0=0.611 \text{ V}$ ).

The substitution of two cyano ligands by bpy in  $\text{W}(\text{CN})_8^{4-}$  ( $E^0=0.51 \text{ V}$  [4, 14]) gives greater changes in the redox potential than those for  $\text{Fe}(\text{bpy})(\text{CN})_4^-$  and  $\text{Ru}(\text{bpy})(\text{CN})_4^-$  (with two cyano ligand substituted), but similar to the complexes for which four cyano groups are substituted. The difference in redox potential between the  $\text{W}(\text{CN})_8^{3-/4-}$  system and the  $\text{W}(\text{bpy})(\text{CN})_6^{-/2-}$  system ( $\Delta E^0=0.335 \text{ V}$ ) corresponds rather well to values for the  $\text{Fe}(\text{CN})_6^{3-/4-}$  and  $\text{Fe}(\text{bpy})_2(\text{CN})_2^{0/+}$  systems ( $\Delta E^0=0.371 \text{ V}$ ) [1, 15]. A similar situation also occurs for the Ru(II,III) analogues [1, 16]. Thus the coordination sphere of octacyanides is more sensitive to incorporation of electron withdrawing polypyridyl than that of the other cyano complexes.

The solvent shift of  $E^0$  is very close to that observed for  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  but much smaller than that of mono-substituted  $\text{Ru}(\text{bpy})(\text{CN})_4^{2-}$  [16]. On the other hand the observed solvent shift is much smaller than that of  $\text{W}(\text{CN})_8^{3-/4-}$  [4] indicating that the solvent interaction with metal is tuned by the  $\pi$ -electron system of the ligand.

#### Electronic absorption spectra

The numerical data of the UV-Vis absorption spectra of  $(\text{AsPh}_4)[\text{W}(\text{bpy})(\text{CN})_6]$  in aqueous and non-aqueous solvents are given in Table 2. For comparison the data for  $(\text{AsPh}_4)_2[\text{W}(\text{bpy})(\text{CN})_6] \cdot 5\text{H}_2\text{O}$  and  $\text{W}(\text{CN})_8^{3-}$  in  $\text{H}_2\text{O}$  are also included. The electronic spectrum of the  $\text{W}(\text{bpy})(\text{CN})_6^-$  ion is similar to that of  $\text{W}(\text{CN})_8^{3-}$ , consisting of three ligand-to-metal charge-transfer (LMCT) bands (at 242, 255 and 357 nm in  $\text{H}_2\text{O}$ ) superimposed with the ligand-field (LF) transitions [17, 18]. The same positions of the lowest energy bands of **A** as for  $\text{W}(\text{CN})_8^{3-}$  indicate that substitution of the cyano ligands by bpy does not significantly change the electron energy levels, which are also LMCT in character. The bands at 356 nm (in  $\text{H}_2\text{O}$ ) seems to be connected with the LMCT  $\text{CN} \rightarrow \text{M}$  transition (by analogy with  $\text{M}(\text{CN})_6^{3-}$ ) whereas the band at 386 nm (in  $\text{H}_2\text{O}$ ) seems to be a LMCT  $\text{bpy} \rightarrow \text{M}$  transition similar to other complexes of that type [1, 19].

The position and intensity of the bands at 356 and 386 nm ( $\text{H}_2\text{O}$ ) are solvent dependent, with a linear correlation between  $\nu_{\text{max}}$  versus Reichardt  $E_{\text{T}}$  parameter [20] (Fig. 3). The small number of solvents used results

TABLE 2. UV-Vis spectral data for (AsPh<sub>4</sub>)[W(bpy)(CN)<sub>6</sub>] (A), (AsPh<sub>4</sub>)<sub>2</sub>[W(bpy)(CN)<sub>6</sub>]·5H<sub>2</sub>O (B) and K<sub>3</sub>[W(CN)<sub>8</sub>] (C) in H<sub>2</sub>O and organic solvents

Complex	Solvent	$\lambda$ (nm) ( $\epsilon \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ )		
		LMCT	MLCT	Others
A	H <sub>2</sub> O	386 sh		312(12), 274(6.4),
		356(2.0)		264(7.2), 244(8.4)
	MeCN	429(0.63)		312(12), 273(8.8),
		365(2.4)		264(9.1), 240(10)
	Me <sub>2</sub> CO	436(0.76)		a
		366(2.1)		
B <sup>b</sup>	H <sub>2</sub> O		565(4.9)	a
			380(2.9)	a
	MeCN		660(9.2)	a
			440(3.9)	
C <sup>c</sup>	H <sub>2</sub> O	357(1.9)		
		255(2.6)		
		242(2.6)		

<sup>a</sup>Only selected data are presented. <sup>b</sup>Data from ref. 3. <sup>c</sup>Data from ref. 17.

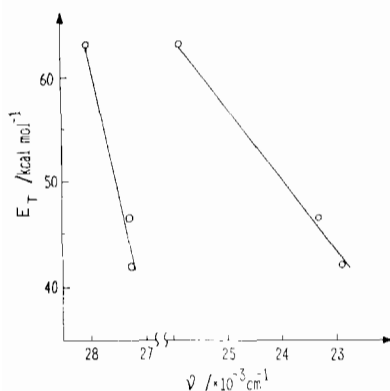


Fig. 3. Plot of  $\nu_{\max}$  vs.  $E_T$  of solvent.

from the decomposition of the complex in many of the solvents studied.

The UV spectrum of A is dominated by two interligand (IL) bands at 312 and 247 nm of coordinated bpy, superimposed with the bands of the cation (at 240, 268, 278 nm) [3] and LMCT bands of the anion.

### Photochemistry

Irradiation within the LMCT band at 365 nm of (AsPh<sub>4</sub>)[W(bpy)(CN)<sub>6</sub>] in aqueous solution results in the formation of the W(bpy)(CN)<sub>6</sub><sup>2-</sup> ion (Fig. 4) with the isosbestic point at 360 nm and characteristic absorbance bands at 380 and 565 nm. The initial quantum yield of the formation of the W(bpy)(CN)<sub>6</sub><sup>2-</sup> ion extrapolated to zero irradiation time is  $\Phi_{365}^0 = 0.17 \pm 0.01$ . The salt formed in light, W(bpy)(CN)<sub>6</sub><sup>2-</sup>, is also light sensitive [21] and upon prolonged photolysis disappearance of the isosbestic point is observed (connected

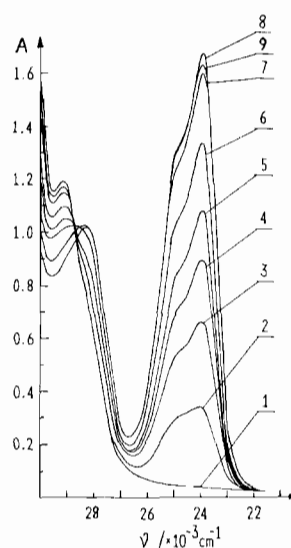


Fig. 4. Continuous photolyses of W(bpy)(CN)<sub>6</sub><sup>2-</sup> in H<sub>2</sub>O:  $d = 1$  cm,  $c = 6.0 \times 10^{-4}$  M,  $\lambda_{ir} = 365$  nm. Irradiation times: 1, 0; 2, 1; 3, 2; 4, 3; 5, 4; 6, 6; 7, 11; 8, 19; 9, 34 min.

with the substitution of the bpy ligand by water (or hydroxy) molecules in W(bpy)(CN)<sub>6</sub><sup>2-</sup>). After longer irradiation this latter process dominates and absorbance at 565 nm starts to diminish with irradiation time (Fig. 4).

The observed pathway of photoreactivity of (AsPh<sub>4</sub>)[W(bpy)(CN)<sub>6</sub>] seems to be similar to the photoreduction of the W(CN)<sub>8</sub><sup>3-</sup> ion with the formation of OH radicals [22].

### Conclusions

The results presented here indicate that the W(bpy)(CN)<sub>6</sub><sup>2-</sup> ion is more similar to W(CN)<sub>8</sub><sup>3-</sup> than to its W(IV) analogue. However it is more thermally and photochemically stable than octacyanotungstate(V). Increase of the redox potential, which is positive in all solvents studied, should simplify the photochemistry of this ion in organic solvents. Thus this salt seems to be promising for further studies on the chemistry and photochemistry of eight-coordinated compounds of W(V), which are now in progress.

### Acknowledgements

The author is grateful to Professor A. Samotus and Professor O. Traverso for helpful discussions. This work was supported by the Polish Research Grants Committee (KBN No. 20677 91 01).

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