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Article

$[PPh_4]_3[W(CN)_7(O_2)]\cdot 4H_2O$ as the Representative of the $[M(L)_7(LL)]$ Class for Nine-Coordinate Complexes

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The photoinduced dissociation of a W–CN bond in $[W(CN)_8]^{4-}$ in an aqueous solution under ambient conditions, in conjunction with the uptake of molecular oxygen, affords the W^{VI} mixed-ligand complex anion $[W(CN)_7(\eta^2\text{-}O_2)]^{3-}$, conveniently isolable as its $[PPh_4^+]$ salt. Although research into the chemistry of cyanomolybdates and cyanotungstates has been pursued with great interest and vigor over several decades, there is a paucity of structurally characterized cyano–peroxo complexes of Mo and W. The side-on coordination mode of the peroxo moiety in $[W(CN)_7(\eta^2\text{-}O_2)]^{3-}$ has been ascertained with X-ray crystal structure determination [d(O–O) = 1.41 Å; peroxo bite angle: 41.0°] and corroborated with vibrational spectroscopy [ν(O–O) = 915 cm^{-1}]. The complex ion exhibits trapezoidal tridecahedral geometry and represents the new class of nine-coordinate complexes with one bidentate and seven monodentate ligands. Cyclic voltammetry shows a reversible redox behavior of $[W(CN)_7(\eta^2\text{-}O_2)]^{3-}$ in CH_3CN with its standard reduction potential equal to 1.130 V. Generally, interest in atmospheric oxygen derives from the versatility of this molecule as a ligand and oxidant and extends to the physicochemical features it imparts to transition metals such as copper and iron in biological oxygen carriers.

Introduction

Despite years of relentless research effort into the chemistry of cyanocomplexes of transition metals, there is still considerable interest in cyanomolybdates and cyanotungstates in part because of their interesting properties and applicability, for instance, as high-temperature magnets and microporous or gas-storage materials.[1] Octacyanocomplexes of Mo(IV) and W(IV) are of particular interest because they are thermodynamically stable and kinetically inert, characteristics that make them amenable to studies of reaction mechanisms. These compounds are known to undergo ligand-field photolysis, and the general mechanism for the photochemical reactions involves generation of hepta- or hexacyanocomplexes as intermediates.[2] The final products of this photolysis are tetracyanooxo- and pentacyanooxometalates; the formation of each of these is dependent on the pH and the concentration of the cyanide ions in the reaction mixture. The crystal structures of these mixed-ligand complexes, as well as those of the starting materials, $[M(CN)_8]^{4-}$ (M = Mo, W), have been determined.[3]

In this work, we report on the synthesis of $[PPh_4]_3[W(CN)_7(\eta^2\text{-}O_2)]\cdot 4H_2O$ effected by the irradiation of an aqueous solution of octacyanotungstate(IV) in the presence of molecular oxygen and the $[PPh_4]^+$ ion. The binding of molecular oxygen by transition-metal complexes is of tremendous importance in that the products act as reagents, catalysts, or key intermediates in selective oxidation reactions. Moreover, small molecules that bind atmospheric oxygen at the metal center can be treated as models for oxygen transport systems in the animal kingdom.[4] Group 6 elements (notably Mo and W) form a considerable number of complexes with dioxygen, most of which bind it as a

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peroxo ligand.[5] However, only a few of these compounds were obtained by the direct incorporation of atmospheric dioxygen; the majority were synthesized using H_2O_2 as the source of the peroxo ligand. The precursor capable of binding O_2(g) was either Mo^{IV} metallooxoporphyrin [MO(por)] (where H_2por = porphyrin or variously substituted porphyrin)[6] or an oxocyanometalate(IV), $[M^{IV}(CN)_4O(L)]^{2-/3-}$ (where M = Mo, W; L = pyrazine, pyridine, or cyanide).[7-10] The strong affinity of these precursors for dioxygen was revealed in the solid state and in organic solvents. The products of reactions with O_2(g), $[Mo^{VI}O(O_2)(por)]$ and $[M^{VI}(CN)_4O(O_2)]^{2-}$, contain a peroxo ligand cis to the oxo in a distorted pentagonal bipyramidal structure.[7-8,11]

Our strategy in this work was stimulated by recent reports on mixed-ligand cyanoperoxocomplexes of Mo and W. Such compounds are still scarce, and to our knowledge, in the group of cyanoperoxocomplexes of Mo(VI) and W(VI), there are only four known isolated species: $[(CN)_5Co^{III}(\mu\text{-}O_2)Mo^{VI}Cl(CN)_5O]^{6-}$ dimer, $[Mo(CN)_3O(O_2)(hmpa)]^-$ (hmpa = hexamethylphosphoramide), $[Mo(CN)_4O(O_2)]^{2-}$, and $[W(CN)_4O(O_2)]^{2-}$.[7-8,12] The latter two complexes were synthesized directly from tetracyano- or pentacyanooxocomplexes of M(IV) and molecular oxygen.[7-10] The aim of this work was to investigate the interactions between dioxygen and the intermediates derived from $[M(CN)_8]^{4-}$ (M = Mo or W).

Experimental Section

Potassium octacyanomolybdate(IV) dihydrate, $K_4[Mo(CN)_8]\cdot 2H_2O$, was synthesized according to a literature method.[13] All other chemicals including buffer solutions were of analytical grade and were used as supplied. Carbon, hydrogen, and nitrogen were determined using a Thermo Finnigan FLASH EA1112 elemental analyzer. Solid samples for IR spectroscopy were compressed as KBr pellets, and the IR spectra were recorded on a JASCO MFT-2000 FT-IR spectrophotometer. Electronic absorption spectra were measured with a Shimadzu UV-3100 scanning spectrophotometer. Diffuse reflectance spectra were measured in $BaSO_4$ pellets with $BaSO_4$ as a reference using a Shimadzu 2101 PC equipped with an ISR-260 attachment. Measurements of electron paramagnetic resonance (EPR) spectra were carried out on a Bruker ELEXSYS spectrometer operating at the X band. The solid samples were examined inside the cavity modulated with a frequency of 100 kHz at −196 °C and at room temperature. Cyclic voltammetry measurements were carried out in CH_3CN and CH_2Cl_2 with $[(C_4H_9)_4N]PF_6$ (0.1 M) as the supporting electrolyte using Pt working and counting and Ag/AgCl reference electrodes on a model EA9 electrochemical analyzer. The redox potentials were reported versus ferrocene, which was used as an internal potential standard for measurements in organic solvents to avoid the influence of the liquid junction potential. $E_{1/2}$ values were calculated from the average anodic and cathodic peak potentials, $E_{1/2} = 0.5(E_a + E_c)$.

Synthesis of $K_4[W(CN)_8]\cdot 2H_2O$ (1).[14] Sodium tungstate(VI) (50.0 g, 0.15 mol), KCN (85.0 g, 1.31 mol), and $NaBH_4$ (10.0 g, 0.26 mol) were dissolved in 150 mL of water. To the stirring solution was added 120 mL of acetic acid (40%) dropwise in two steps: 24 mL within a period of 1 h and the rest within half an hour. The resultant light-green solution was treated with H_2O_2 (30%), which was added dropwise until the color changed to orange, and then ethanol (ca. 150 mL) was added. The yellow precipitate of **1** (yield: 61.4 g, 70%) was filtered off, washed with ethanol, and then dried in the air at room temperature. The purity was confirmed by IR and UV−vis spectra.

Synthesis of $[PPh_4]_3[W(CN)_7(O_2)]\cdot 4H_2O$ (2). To a stirring buffered solution (4.0 mL, pH = 7) of $K_4[W(CN)_8]\cdot 2H_2O$ (11.7 mg, 0.020 mmol) was added an aqueous solution (2.0 mL) of tetraphenylphosphonium chloride (24.0 mg, 0.064 mmol). Then, the reaction mixture was exposed to diffused visible light under ambient conditions for one fortnight, during which time orange crystals of **2** (yield: 17.5 mg, 59%) were deposited. The crystals were filtered off, washed with water, and dried in the air at room temperature. Anal. Calcd for $C_{79}H_{68}N_7O_6P_3W$: C, 63.76; H, 4.61; N, 6.59. Found: C, 64.33; H, 4.36; N, 6.69%. IR (KBr, cm^{-1}): υ_{OO} 915 (m), υ_{CN} 2146 (s), 2204 (w).

Crystallographic Data Collection and Structure Refinement

Orange crystals of $[PPh_4]_3[W(CN)_7(O_2)]\cdot 4H_2O$ (**2**) suitable for X-ray analysis were selected from the material prepared as described in the Experimental Section. Intensity data were collected on a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo Kα radiation. The crystal data and details of data collection and structure refinement are summarized in Table 1. The positions of the W and P atoms were determined by direct methods, but the rest of the non-hydrogen atoms were located in successive difference Fourier syntheses. The largest peaks in the final difference map were located near heavy atoms. Because the hydrogen atoms of two water molecules (O5 and O6) were not located on difference Fourier maps, they were not included in the refinement. All other hydrogen atoms were included in the structure factor calculations at idealized positions. All non-hydrogen atoms were refined anisotropically. Calculations were performed using a

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(14) The synthesis of $K_4[W(CN)_8]\cdot 2H_2O$ (**1**) is the improved method of its preparation given in the literature by Leipoldt et al.[15] First of all, the amount of KCN required per tungsten was considerably reduced to an almost stoichiometric ratio (from 20:1 to 8.7:1). It is very important because the excess of KCN must be removed from the system in an acidic medium as HCN during the synthesis. It has also been observed that the addition of H_2O_2 is required to obtain the pure product, not contaminated with impurities mentioned in the literature method (crude product was treated with animal charcoal). The amount of H_2O_2 depends on KCN and $NaBH_4$ concentrations as well as other synthesis details such as the temperature and time period of acid addition. The yield is very reproducible and comparable to that given in the Leipoldt method.

Table 1. Crystal Data and Structure Refinement Parameters for $[PPh_4]_3[W(CN)_7(O_2)]\cdot 4H_2O$ (**2**)

empirical formula	$C_{79}H_{68}N_7O_6P_3W$
fw	1488.15
cryst size (mm)	$0.58 \times 0.28 \times 0.13$
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	13.1951(11)
b (Å)	13.9814(12)
c (Å)	21.5885(18)
α (deg)	77.8710(10)
β (deg)	87.181(2)
γ (deg)	62.9770(10)
V (Å^3)	3463.9(5)
Z	2
T (K)	291(2)
D_{calcd} (Mg/m^3)	1.427
λ (Å)	0.71073
μ (mm^{-1})	1.796
reflns measured	21526
reflns unique	15266
reflns observed [$I > 2\sigma(I)$]	12816
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0336$ $wR_2 = 0.0841$

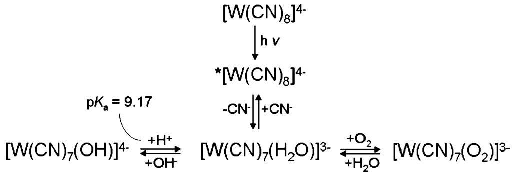
SHELXTL software package.[16] Crystallographic data are available in CIF format in the Supporting Information, and full crystallographic data may be obtained from the Cambridge Crystallographic Data Centre. The CCDC reference number is X.

Results and Discussion

Remarks to the Synthesis of $[PPh_4]_3[W(CN)_7(O_2)]\cdot 4H_2O$ (2). Previously, we have observed that both anaerobic and aerobic irradiation of an aqueous solution of octacyanotungstate(IV) with visible light under appropriate conditions leads primarily to the release of a cyano ligand. The resultant heptacyano intermediates are readily converted to penta- or tetracyanooxotungstates(IV) in high-intensity light, whereas in the darkness, they are converted reversibly to the original octacyanotungstate(IV). Our previous investigations have shown that pentacyanooxo species coexist in substitutional equilibrium with tetracyanooxo ions and that these photoproducts with a smaller number of cyano ligands (four or five) have an affinity for molecular oxygen.[8,10] Therefore, in the synthesis of $[W(CN)_7(\eta^2\text{-}O_2)]^{3-}$, we used diffused light of low intensity or ordinary sunlight in order to control the photodissociation and prevent uncontrolled photodecomposition. The low-intensity light was also found to be essential for the formation of high-quality crystals of **2** for X-ray diffraction. Intense photolyses result in the formation of **2** in low yields as a consequence of photodecomposition.

A general reaction summary for the ligand-field photolysis of an aqueous solution of octacyanotungstate(IV) is shown in Scheme 1. The oxygenated and oxidized photoproduct, $[W(CN)_7(\eta^2\text{-}O_2)]^{3-}$, is isolated as its tetraphenylphosphonium salt. Evidently, the crucial conditions for the synthesis and isolation of $[PPh_4]_3[W(CN)_7(O_2)]\cdot 4H_2O$, **2**, include the presence of light of appropriate intensity and energy, molecular oxygen, an appropriate counterion and optimum pH of the solution. The appropriate pH range is modulated by the value of the dissociation constant for the heptacyanoaqua complex ion, $[W(CN)_7(O_2)]^{3-}$ ($pK_a = 9.17$).[17] The substitution of the aqua ligand in heptacyanoaquatungstate(IV) has previously been demonstrated with 1,4-diazine.[18] When the irradiation was carried out either in strongly alkaline solution (pH = 13.0) or under argon, no product was precipitated even in the presence of bulky aromatic cations. The pH conditions show that the aqua ligand is labile toward oxidative substitution with dioxygen.

Scheme 1. Synthetic Route to $[W(CN)_7(\eta^2\text{-}O_2)]^{3-}$



The UV−vis spectra recorded during the aerobic photolysis of solutions (pH = 7) free of any counterion exhibition are indistinguishable from that observed for the solution under an inert atmosphere.[19] This suggests that, in the absence of $[PPh_4]^+$, the desired product is either not formed at all or formed in minute amounts spectroscopically undetectable. Clearly, the $[PPh_4]^+$ ion stabilizes the complex ion $[W(CN)_7(\eta^2\text{-}O_2)]^{3-}$, isolable as $[PPh_4]_3[W(CN)_7(O_2)]\cdot 4H_2O$.

The isolated orange photoproduct **2** is stable in the air and in polar organic solvents such as methanol, ethanol, acetonitrile, dichloromethane, and DMF. It is insoluble in water, THF, *n*-hexane, 2-propanol, acetone, and xylenes. In an ethanol−water mixture (1:1, v/v), **2** was observed spectroscopically to react with cyanides, giving the octacyanotungstate(IV) ion. The extent of this process (ca. 50%) was confirmed spectrophotometrically by monitoring the increasing intensity of the characteristic absorption bands of $[W(CN)_8]^{4-}$.

All attempts to obtain the molybdenum analogue under similar conditions proved to be unsuccessful probably because of a considerable difference in the redox potentials of $[M(CN)_8]^{3-}/[M(CN)_8]^{4-}$ couples. It is more difficult to oxidize Mo(IV) octacyanide than its W(IV) analogue [$E° = 0.78$ V (Mo), 0.51 V (W)].[20]

Structure. The structure of $[W(CN)_7(\eta^2\text{-}O_2)]^{3-}$ is presented in Figure 1, and the selected bond lengths and angles are given in Table 2.

The coordination number of tungsten in $[W(CN)_7(O_2)]^{3-}$ is nine. Up until now, four types of nine-coordinate complexes in general have been reported: $[M(L)_9]$, $[M(LL)_3(L)_3]$, $[M(LL)_4(L)]$, and $[M(LLL)_3]$ (where L is monodentate, LL bidentate, and LLL tridentate); $[W(CN)_7(O_2)]^{3-}$ represents the first member of the $[M(LL)(L)_7]$ class.[21,22] The donor

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$[PPh_4]_3[W(CN)_7(O_2)]\cdot 4H_2O$

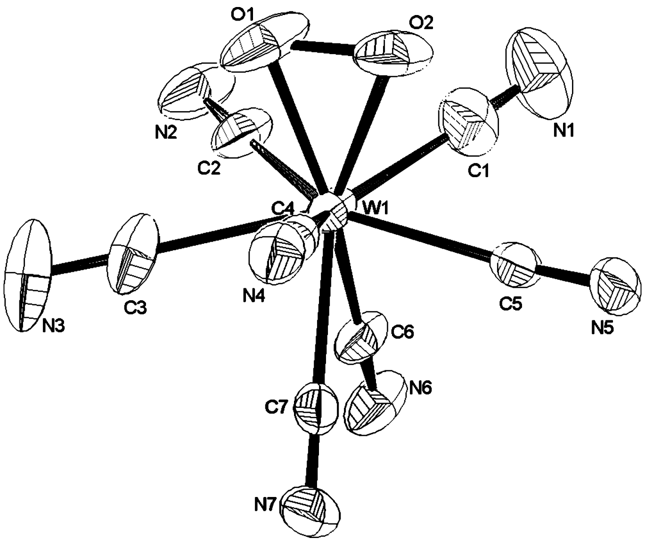

Figure 1. Structure of the complex anion $[W(CN)_7(O_2)]^{3-}$ with the atom labeling scheme and 30% displacement ellipsoids.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[PPh_4]_3[W(CN)_7(O_2)]\cdot 4H_2O$ (**2**) with Estimated Standard Deviations in Parentheses

	Bond Lengths		
W1−O1	2.009(2)	O1−O2	1.412(4)
W1−O2	2.019(2)	C1−N1	1.130(6)
W1−C1	2.193(5)	C2−N2	1.141(5)
W1−C2	2.183(4)	C3−N3	1.142(5)
W1−C3	2.166(4)	C4−N4	1.137(5)
W1−C4	2.210(4)	C5−N5	1.140(4)
W1−C5	2.162(3)	C6−N6	1.144(4)
W1−C6	2.187(3)	C7−N7	1.144(4)
W1−C7	2.184(3)		
	Bond Angles		
O1−O2−W1	69.10(15)	N3−C3−W1	178.8(5)
O2−O1−W1	69.86(15)	N4−C4−W1	178.5(3)
O1−W1−O2	41.05(13)	N5−C5−W1	175.7(3)
N1−C1−W1	177.7(5)	N6−C6−W1	178.6(3)
N2−C2−W1	178.5(4)	N7−C7−W1	178.0(3)

atoms in the complex anion of **2** occupy the vertexes of a tridecahedron with one trapezoidal and 12 triangular faces. The anion adopts a stereochemistry that cannot be recognized as belonging to any of the five convex polyhedra with nine vertexes and regular faces. These are nonuniform polyhedra: tricapped trigonal prism (triaugmented triangular prism); capped square antiprism (gyroelongated square pyramid); triangular cupola; capped cube (elongated square pyramid); and tridiminished icosahedron.[23] Because of prohibitively high repulsion energies between metal−ligand bonds in the latter three arrangements,[22,24] we have considered the two most stable geometries (tricapped trigonal prism and capped square antiprism) to be relevant to **2**. The three various projections of the polyhedron in **2** are shown in Figure 2, and the comparison of its dihedral angles with the idealized ones is presented in Table 3. This comparison shows that the dihedral angles in **2** are very different from those of a tricapped trigonal prism and a capped square antiprism. The considerable deviations of the dihedral angles of **2** from the idealized ones are the result of the presence of the bidentate peroxide with a very small bite angle (41.0°). Thus, the structure of the anion can be described generally as a trapezoidal tridecahedral one taking into account the presence of one distorted trapezoidal face in the coordination polyhedron.

Table 3. Dihedral Angles in Nine-Coordination for Idealized Polyhedra and Complex Ion of $[PPh_4]_3[W(CN)_7(O_2)]\cdot 4H_2O$ (**2**)

	number of edges	dihedral angles (deg)	corresponding angles (deg) in **2** observed		average
tricapped trigonal prism	3	169.5	131.6 152.8	169.8	151.4
	6	144.7	118.9 125.9 126.8	134.8 140.4 144.2	131.8
	12	109.5	107.9 109.7 113.5 116.3 119.5 121.4	122.2 123.7 123.9 125.9 132.4 134.3	120.9
capped square antiprism	4	158.6	126.8 131.6	144.2 152.8	138.9
	8	127.5	113.5 118.9 121.4 125.9	132.4 134.3 134.8 140.4	127.7
	4	109.5	109.7 119.5	123.9 125.9	119.7
	4	103.8	107.9 116.3	122.2 123.7	117.5

The O−O bond distance of 1.41 Å is typical for the peroxo ligand, and thus, the formal oxidation state of tungsten is +6.[4,25] The oxygen atoms of O_2^{2-} are equidistant from the metal center ($d_{W1-O1} = 2.01$ Å and $d_{W1-O2} = 2.02$ Å). The peroxo ligand is located farther from the metal atom by ~0.1 Å, and the O−O bond is shorter by ~0.04 Å compared to the related tetracyanooxoperoxotungstate(VI) (Figure 3).[26] This could be attributed to greater steric hindrance and higher repulsion energies between metal−cyano and metal−peroxo bonds in the nine-coordinate complex. The distance of the peroxo ligand from the metal center is consistent with the smaller bite angle in **2** (41.0°; cf. 43.1° for Mo and 44.5° for W in $[M(CN)_4O(O_2)]^{2-}$). The slightly shorter O−O bond in **2** (1.41 Å) compared with that in $[W(CN)_4O(O_2)]^{2-}$ (1.45 Å) indicates its higher potential reactivity as an oxidant in radical processes rather than in reactions with oxygen atom transfer.[27] The W1−C and C−N bond lengths are normal (averages: $d_{W1-C} = 2.184$ Å and $d_{C-N} = 1.140$ Å), and the W1−C−N groups are approximately linear (the average W1−C−N angle is 178.0°).[28] The structure is stabilized by two main hydrogen-bonding groups. One group involves four hydrogen bonds linking water oxygens to cyanide nitrogens (O3−N7, O3−N4′, O5−N2′, and O6−N1, with O−N

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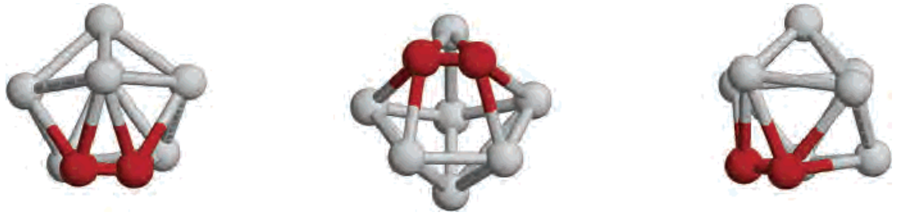

Figure 2. Tridecahedral geometry of the complex anion in $[PPh_4]_3[W(CN)_7(O_2)]\cdot 4H_2O$ (**2**).

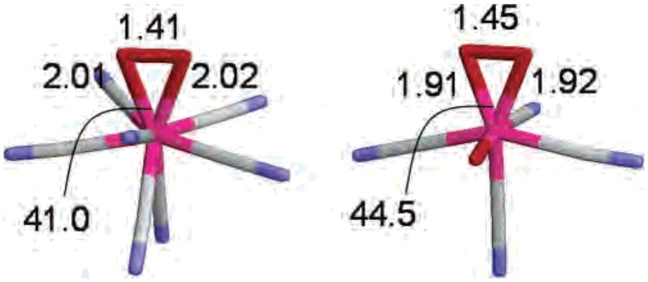

Figure 3. Comparison of selected structural features [bond lengths (Å) and angles (deg) within MOO group] between $[PPh_4]_3[W(CN)_7(O_2)]\cdot 4H_2O$ (**2**) and tetracyanooxoperoxotungstate(VI).

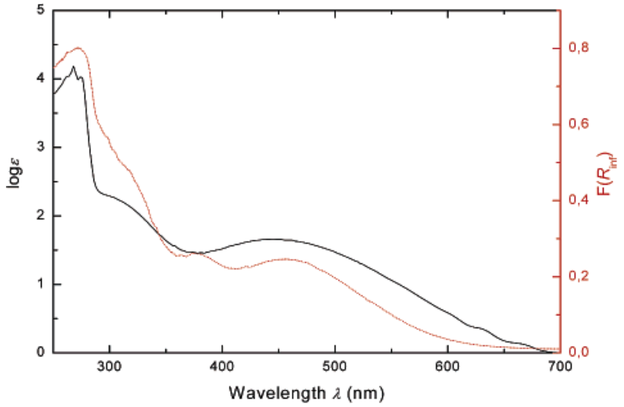

Figure 4. UV−vis spectrum of $[PPh_4]_3[W(CN)_7(O_2)]\cdot 4H_2O$ (**2**) in MeCN (solid line). For comparison, the diffuse reflectance (red line) spectrum is given.

distances of 2.983, 2.969, 2.842, and 3.045 Å, respectively), and the other contains two hydrogen bonds between water oxygens: O3−O4 (2.747 Å) and O4−O4′ (2.899 Å).

Spectroscopic Properties. The IR spectrum of **2** exhibits an absorption band at 915 cm^{-1} assignable to the stretching vibrations of the peroxo group bonded side-on.[25,29] The absorption of ν(O−O) in **2** is considerably higher in energy than that observed in $[PPh_4]_2[W(CN)_4O(O_2)]$ (871 cm^{-1}), indicating that the O−O bond in **2** is the stronger one.[8] This is consistent with this bond being shorter. In the C−N stretching region, the IR spectrum shows bands at 2146w and 2204vw cm^{-1}. Their positions are similar to those observed in $[PPh_4]_2[W(CN)_4O(O_2)]$ (2132vvw, 2154vvw, and 2201vvw cm^{-1}).[8] The higher energy of these absorptions in comparison with those of ν(C−N) in related cyanocomplexes of W(IV) (2050−2150 cm^{-1}) can be explained in terms of the decrease of π back-donation upon an increase of the formal oxidation state of the central atom, which shifts the C−N stretching band toward higher energy. The spectrum shows also bands characteristic for $[PPh_4]^+$ cations.

The reflectance and solution UV−vis spectra (Figure 4) of **2** contain $\pi-\pi^*$ high-intensity charge-transfer bands within tetraphenylphosphonium cations in the UV region (<280 nm) as well as bands of relatively low intensity assigned to ligand-to-metal charge-transfer bands. The ligand-to-metal charge transfer (LMCT) band (λ = 445 nm, ϵ = 46 $dm^3\ mol^{-1}\ cm^{-1}$ in MeCN) may be assigned to a transition between peroxide π^* and d orbitals of metal. The low-energy LMCT band of this origin was also observed in other peroxocomplexes of d^0 complexes.[8,27]

The qualitative EPR measurements carried out in the solid state revealed only approximately four promiles of paramagnetic centers in the analyzed sample. The signal of similar intensity appears in solution (MeCN). It confirms the diamagnetism of **2** and is consistent with the assignment of formal oxidation state +6 for the metal center as well as with the presence of molecular oxygen in the form of the peroxo ligand. The number of paramagnetic centers in tetracyanoxomolybdates and -tungstates(VI) was also found to be lower than 1%.[8] The existence of paramagnetic centers indicates that to some extent thermal electron transfer from the O_2^{2-} ligand to the metal occurs, resulting in W(V) and O_2^- formation, as it was also observed in the $[M(CN)_4O(O_2)]^{2-}$ systems.

The cyclic voltammograms of **2** were recorded in acetonitrile at various scan speeds (20−500 mV s^{-1}) over the range from −1400 to 2400 mV. It has been found that the complex can be reversibly reduced and oxidized, with symmetrical oxidation and reduction peaks whose positions were independent of the scan speed. The oxidation and reduction peaks separation was found to be 59 mV, which corresponds to a one-electron process. The standard redox potential for the $[W(CN)_7(O_2)]^{3-}/[W(CN)_7(O_2)]^{4-}$ couple was determined as 1.130 V. This relatively high potential indicates that complex **2** is the strong oxidant. The oxidation activity of **2** will be the subject of further study.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http:://pubs.acs.org. Full crystallographic data may be obtained from the Cambridge Crystallographic Data Centre. The CCDC reference number is CCDC 616560.

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