Eightfold Electrophilic Methylation of Octacyanotungstate $[W(CN)_8]^{4-/3-}$: Preparation of Homoleptic, Eight-coordinate Methylisocyanide Complexes $[W(CNMe)_8]^{4+/5+}$

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ABSTRACT: Homoleptic eight-fold coordinated methylisocyanide complexes of W(IV) and W(V) have been prepared for the first time. The reaction of $[NBu_4]_4[W(CN)_8]$ with methyl triflate MeOTf gives $[W(CNMe)_8][OTf]_4$. The even stronger methylating mixture of methyl fluoride MeF and arsenic pentafluoride AsF_5 in liquid sulfur dioxide SO_2 is able to fully alkylate both $[NBu_4]_4[W(CN)_8]$ and $[NBu_4]_3[W(CN)_8]$. The paramagnetic octakis(methylisocyanide)-tungsten(V) $[W(CNMe)_8][AsF_6]_5$ is thermally highly unstable above −30 °C. All compounds have

been characterized via single-crystal X-ray diffraction, IR and Raman, as well as NMR or EPR spectroscopy.

INTRODUCTION

Similarly, to carbonyl ligands, isocyanides (C≡N-R) are good ligands for metals in low oxidation states. Due to the weaker π-accepting properties of isocyanides in comparison with carbonyl (CO) ligands, there exist only very few examples of homoleptic metal-isocyanide complexes with metals in negative oxidation states $[M(CNR)_6]^-$ (for M=V, Nb, Ta),[1] $[Fe(CNR)_4]^{2-}$ [2] and $[Co(CNR)_4]^-$.[3] In comparison with cyanide ligands, the σ-donating properties of alkyl isocyanide ligands are less pronounced, which is a limiting factor for the stability of metal alkyl isocyanide complexes in high oxidation states.

While thousands of molybdenum and tungsten complexes with isocyanides as co-ligands (M−C≡N-R) exist, homoleptic complexes are scarce. Although known since the 1970s, complexes $[M(CNR)_6]$ containing aryl isocyanide groups and zerovalent Cr, Mo and especially W have recently gained some attention due to their attractive properties as very strong photoreductants and their low cost compared to ruthenium or iridium compounds.[4] In presence of an oxidant and an excess of isocyanide RNC, complexes $[M(CNR)_7]^{2+}$ can be prepared. For example, $[Mo(CNMe)_7]^{2+}$ was prepared by the oxidation of $[Mo(CO)_6]$ with elemental iodine in presence of an excess methyl isocyanide.[5] These compounds represent rare examples of homoleptic seven-coordinate complexes.

The number of structurally characterized group 6 metal complexes with seven isocyanide ligands is very limited. The crystal structures of $[Mo(CN^tBu)_7][PF_6]_2$,[6] $[W(CN^tBu)_7][W_6O_{19}]$,[7]

$[W(CN^tBu)_7][PF_6]_2$,[8] and $[Mo(CNMe)_7][BF_4]_2$ [9] have been reported in the 1970s and beginning 1980s. For the latter, the corresponding tungsten compound is only briefly mentioned in the literature.[10] For molybdenum, also the crystal structures of $[Mo(CNR)_7][PF_6]_2$ are known (R= cyclohexyl, phenyl).[8, 11] Interestingly, also a seven-coordinate chromium complex $[Cr(CN^tBu)_7][PF_6]_2$ exists.[12]

In contrast, octacyanometalates $[M(CN)_8]^{4-/3-}$ (M= Mo, W) have been frequently used as building blocks in coordination chemistry.[13] Most relevant are their applications in magnetochemistry,[14] for example for the preparation of photomagnetic materials[15] and single-molecule magnets.[16]

Since octacyanometallates $[M(CN)_8]^{4-/3-}$ (M = Mo, W) are known, the question arises whether it could be possible to synthesize the fully alkylated complexes with eight isocyanide ligands, as 18-valence electron complexes $[M(CNR)_8]^{4+}$ would be the logical missing link in the series $[M(CNR)_6]$ and $[M(CNR)_7]^{2+}$ complexes (M = Mo, W). First attempts date to the end of the 1920s when Hölzl studied the reaction between methyl iodide MeI and $Ag_4[Mo(CN)_8]$/$Ag_4[W(CN)_8]$.[17] Unfortunately, he was not able to determine the correct structure due to the lack of suitable spectroscopic methods. Almost 40 years later, Latka reported that this reaction gives $[W(CN)_4(CNMe)_4]\cdot 2\ H_2O$.[18] Soon after, the triangular-dodecahedral structure of $[Mo(CN)_4(CNMe)_4]$ in the solid state and other alkylated derivatives were reported.[19] Lippard *et al.* reported that a mixture of $Ag_4[Mo(CN)_8]$ and AgCN reacted with an excess of *tert*-butyliodide in chloroform to give $[Mo(CN^tBu)_7][I_3]_2$ after workup.[20]

To achieve eightfold methylation, it seemed necessary to choose a drastically more powerful methylating agent. Recently, we reported that eight-fold protonation of $[M(CN)_8]^{4-}$ (M=Mo, W) to the corresponding $[M(CNH)_8]^{4+}$ tetracations is achieved under superacidic conditions by a combination of anhydrous hydrogen fluoride with the super Lewis acid SbF_5.[21] Similarly, the combination of MeF with AsF_5 in liquid SO_2 as solvent is known to generate the extremely powerful methylating agent $[MeOSO][AsF_6]$.[22] However it has been rarely used in recent times.[23]

EXPERIMENTAL SECTION

$K_4[W(CN)_8]\cdot 2\ H_2O$ was prepared according to the literature procedure.[24] Tetrabutylammonium chloride, tetrabutylammonium hydroxide 40% w/w in water, Amberlyst 15 hydrogen form, methyl triflate and methyl fluoride were purchased from commercial sources and used without further purification. Sulfur dioxide (Attention: toxic gas with boiling point of −10 °C, high vapor pressure) was dried over calcium hydride and stored in a stainless-steel gas cylinder. AsF_5 was prepared by literature procedures and stored in a stainless-steel gas cylinder.[25] AsF_5 is a highly toxic and corrosive gas (boiling point −53 °C, Attention: high vapor pressure) that should be only handled by trained personal with suitable protective equipment. For condensing in methyl fluoride (boiling point −78 °C, vapor pressure of 33 bar at room temperature (!)) as well as AsF_5, the gas cylinders were placed in cold ethanol baths to reduce the overpressure. Strong alkylating agents (e.g. methyl triflate) are potentially carcinogenic.

Tetrabutylammonium octacyanotungstate(IV) $[NBu_4]_4[W(CN)_8]$:

An acidic ion exchange resin (Amberlyst 15 hydrogen form) (3 g) was filled in a Schlenk flask and degassed water (24 mL) was added. After the addition of potassium octacyanotungstate(IV) dihydrate (1 g, 1.71 mmol, 1 eq.) the solution was stirred for a few minutes. 18 mL of the solution were decanted off and transferred to another Schlenk flask and the solution was neutralized with 40% w/w $[NBu_4]OH$ in water (3.3 g, 5.10 mmol, 2.98 eq.). The water was removed under vacuum and the residue was taken up in degassed dichloromethane (5 mL), which was removed under vacuum afterwards. The crude product was washed with degassed diethyl ether (3x 5 mL) to remove traces of the octacyanotungstate(IV) acid and dried under high vacuum to remove traces of solvent. The product was obtained as a fine bright-yellowish powder and stored under argon.

Yield: 1.65 g, 1.21 mmol, 71% (based on the octacyanotungstate). IR (ATR, in cm^{-1}): $\tilde{\nu}$ = 2960 s, 2937 s, 2875 s, 2128 sh, 2086 m, 1665 w, 1488 s, 1459 sh, 1382 m, 1214 w, 1154 m, 1090 m, 1027 w, 883 m, 799 w, 734 m, 692 w. Raman (1064 nm, in cm^{-1}): $\tilde{\nu}$ = 2960 sh, 2922 s, 2874 s, 2144 sh, 2119 s, 2093 sh, 2080 sh, 1479 m, 1461 m, 1320 w, 1129 w, 1059 m, 905 m, 156 m, 63 m.

Octakis(methylisocyanide)tungsten(IV) triflate $[W(CNMe)_8][OTf]_4$:

$[NBu_4]_4[W(CN)_8]$ (460 mg, 338 µmol, 1 eq.) was dissolved in dichloromethane (3 mL) and methyl triflate (0.69 g, 0.46 mL, 4.2 mmol, 12.4 eq.) was slowly added. The solution was stirred over two days and was filtered. The residue was carefully washed with dichloromethane (3x 2 mL). The product was obtained as a yellowish powder.

Single crystals of $[W(CNMe)_8][OTf]_4$ suitable for X-ray diffraction could be obtained after one day by vapor diffusion of diethyl ether into an acetonitrile solution of the product at room temperature (CCDC 2058758).

Yield: 270 mg, 244 µmol, 72%. IR (ATR, in cm^{-1}): $\bar{\nu}$ = 3026 w, 2959 w, 2272m, 1439w, 1309w, 1260s, 1226m, 1199m, 1150s, 1030s, 932w, 754w, 636s, 573m, 516m, 463m. Raman (1064 nm, in cm^{-1}): $\tilde{\nu}$ = 2957 s, 2282 s ^{1}H-NMR (700 MHz, CD_3CN, 25 °C): δ = 3.85 (s, CH_3). ^{13}C (176 MHz, CD_3CN, 25 °C): δ = 31.82 (CN**Me**), 115.30 (**C**NMe). ^{15}N HMQC (700/71 MHz, CD_3CN, 25 °C): δ = 140 (C**N**Me, reference: NH_3). ^{19}F (377 MHz CD_3CN, 25 °C): δ = −79.21 (OTf).

Octakis(methylisocyanide)tungsten(IV) hexafluoroarsenate $[W(CNMe)_8][AsF_6]_4$:

$[NBu_4]_4[W(CN)_8]$ (180 mg, 135 µmol, 1 eq.) was filled in an 8 mm PFA tube. Sulphur dioxide (0.5 mL), methyl fluoride (96 mg, 2.8 mmol, 21 eq.) and arsenic pentafluoride (250 mg, 1.47 mmol, 11 eq.) were condensed at −196 °C in the reaction tube. The reaction mixture was held for one hour at −78 °C and then carefully brought to room temperature (Attention: overpressure) and the volatiles were removed under vacuum. The residue was washed with dichloromethane (2x 2 mL) and dried under high vacuum and stored under argon.

Single crystals of $[W(CNMe)_8][AsF_6]_4 \cdot 3$ MeCN suitable for X-ray diffraction could be obtained after one day by vapor diffusion of diethyl ether into an acetonitrile solution of the product at room temperature (CCDC 2058764).

Yield: 131 mg, 103 µmol, 76%. IR (ATR, in cm^{-1}): $\tilde{\nu} = 2964$ w, 2276 m, 1436 w, 1407 w, 893 m, 693 s, 481 w, 465 w. Raman (1064 nm, in cm^{-1}): $\tilde{\nu} = 2968$ s, 2305 s, 2289 s, 1404 m, 681 m. ^{1}H NMR (700 MHz, CD_3CN, 25 °C): $\delta = 3.85$. ^{13}C (176 MHz, CD_3CN, 25 °C): $\delta = 31.82$, 115.30. ^{19}F NMR (377 MHz, CD_3CN, 25 °C): $\delta = -66.06$ (q, $^{1}J_{75As-19F} = 932$ Hz).

Tetrabutylammonium octacyanotungstate(V):

Potassium octacyanotungstate(IV) dihydrate (500 mg, 856 mmol, 1 eq.) was dissolved in water (2 mL) and aqueous 65% nitric acid (2.4 mL) was added. Tetrabutylammonium chloride (910 mg, 2.83 mmol, 3.3 mmol) was dissolved in water (5 mL). The two solutions were combined, the colorless precipitate was filtered off and washed with water (2x5 mL) and diethyl ether (2x5 mL). The crude product was dried under high vacuum.

Yield: 945 mg, 844 µmol, 98%. IR (ATR, in cm^{-1}): $\tilde{\nu}$ = 2960 s, 2938 sh, 2875 s, 2143 w, 2124 w, 1488 s, 1460 s, 1383 s, 1154 m, 1029 m, 882 s, 754 w, 733 m. Raman (1064 nm, in cm^{-1}): $\tilde{\nu}$ = 2969 sh, 2930 s, 2975 s, 2733 w, 2144 s, 2134 sh, 1482 m, 1450 m, 1321 w, 1133 w, 1057 w, 906 w, 397 w, 154 m, 67 m.

Octakis(methylisocyanide)tungsten(V) hexafluoroarsenate $[W(CNMe)_8][AsF_6]_5$:

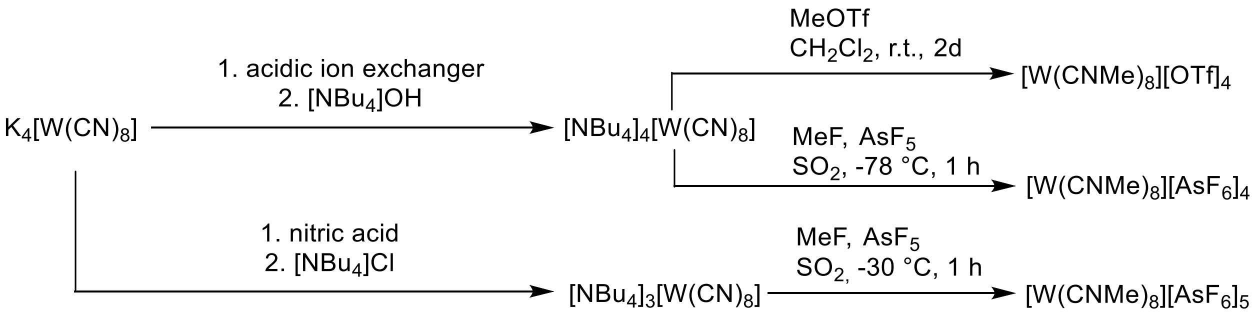
$[NBu_4]_3[W(CN)_8]$ (24 mg, 21.4 µmol, 1 eq.) was filled in an 8 mm PFA tube. Sulphur dioxide (1 mL), methyl fluoride (50 mg, 1.47 mmol, 73 eq.) and arsenic pentafluoride (39 mg, 200 µmol, 9.3 eq.) were condensed at −196 °C in the reaction tube. The reaction mixture was carefully brought to −30 °C for one hour (thermal decomposition above −30 °C) and occasionally mechanically shaken to give a yellow-brown solution (Attention: overpressure). Subsequently, the mixture was frozen with liquid nitrogen and the tube was flame-sealed under vacuum. The tube was placed in a dewar with cold ethanol (−30 °C) and placed in a −80 °C freezer. After several days, yellow single crystals of $[W(CNMe)_8][AsF_6]_5 \cdot 5\ SO_2$ formed, which were decanted in the cold and selected under a microscope in a cold nitrogen stream (CCDC 2058769). Additionally, the crystals were transported to an ATR IR spectrometer where the sample was measured at −30 °C. Similarly, a Raman spectrum was recorded of a signal crystal using a Raman microscope at liquid nitrogen temperature.

IR (ATR, −30 °C, in cm^{-1}): $\tilde{\nu}$ = 2970 w, 2284 s, 1442 w, 934 w, 696 s. Raman (1064 nm, −196 °C, in cm^{-1}): $\tilde{\nu}$ = 2957 m, 2307 s, 1408 m, 1150 m, 682 m. X-band EPR (frozen solution in SO_2, −196 °C): $g_{\parallel} = 1.9815$, $g_{\perp} = 1.9685$, $A_{\parallel}^{W} = 25 \cdot 10^{-4}$ cm^{-1}, $A_{\perp}^{W} = 65 \cdot 10^{-4}$ cm^{-1}.

RESULTS AND DISCUSSION

Synthesis

Due to the insolubility of $K_4[W(CN)_8]\cdot 2\,H_2O$ in organic solvents, the corresponding tetrabutylammonium salt $[NBu_4]_4[W(CN)_8]$ was chosen as a suitable starting material. This air-sensitive compound was prepared (analogously to the tetrapropylammonium salt)[26] by treatment of the potassium salt with an acidic ion exchange resin in water, followed by neutralization with tetrabutylammonium hydroxide until the clear aqueous solution was neutral (Scheme 1). Vacuum-dried $[NBu_4]_4[W(CN)_8]$ was reacted with an excess of methyl triflate in dichloromethane at room temperature for two days. The insoluble product was filtered off. Due to the long reaction times and the formation of side-products, we looked for an alternative procedure for alkylation. The reaction time can be reduced to under one hour at −78 °C by using the powerful methylating agent $[MeOSO][AsF_6]$ (prepared from methyl fluoride MeF and arsenic pentafluoride AsF_5 in sulfur dioxide)[22] and the formation of side products is less pronounced. As octacyanotungstate exists both in the tetra- and pentavalent state, we wondered if also $[W(CN)_8]^{3-}$ could be fully methylated. $[NBu_4]_3[W(CN)_8]$ is easily accessible via the oxidation of potassium octacyanotungstate(IV) in water with nitric acid,[27] followed by precipitation with tetrabutylammonium cations in water. The following methylation with MeF and AsF_5 in sulfur dioxide must remain under −30 °C due to the high temperature sensitivity of the resulting product $[W(CNMe)_8][AsF_6]_5$.



Scheme 1. Preparation of tetrabutylammonium salts of the octacyanotungstate(IV/V) anions and electrophilic methylation to the corresponding homoleptic isocyanide complexes.

Crystal Structures

$[W(CNMe)_8][OTf]_4$ crystallizes in the monoclinic space group $P2_1/n$. Although the triflate counterions are disordered, the structure of the $[W(CNMe)_8]^{4+}$ is well resolved. In general, the coordination geometry of eight-coordinate metal ions is quite complex, since various geometries are possible that vary only little in energy.[26, 28] Since also intermediate geometries are possible, the coordination geometry of an eight-coordinate metal is best described by continuous shape measurements with the software SHAPE 2.1.[29] Here, the structure of $[W(CNMe)_8]^{4+}$ resembles more a square-antiprism (CShM = 0.49) than a triangular dodecahedron (CShM = 1.44). The W-C bond lengths are in the range of 2.141(6)-2.153(6) Å while C-N distances vary between 1.128(8)-1.137(7) Å (C≡N) and 1.428(8)-1.445(8) Å (N-Me). These values are similar to bond lengths in $K_4[W(CN)_8]\cdot 2\ H_2O$ (W-C 2.142-2.182 Å, C≡N 1.121-1.159 Å).[30] The positively polarized hydrogen atoms of the methyl groups form hydrogen bonds to oxygen atoms of the triflate counterions (H···O distances 2.3-2.7 Å).

$[W(CNMe)_8][AsF_6]_4 \cdot 3$ MeCN crystallizes in the monoclinic space group *Cc*. The W-C (2.139(5) and 2.162(5) Å), C≡N (1.132(7)-1.145(6) Å) and N-CH_3 (1.435(7)-1.445(6) Å) bond lengths are similar to the structure of the corresponding triflate salt (Figure 1). Relatively short H···F contacts between 2.1 and 2.7 Å are observed between the methyl protons of the tetracation and the hexafluoroarsenate anions. Here, the coordination geometry of $[W(CNMe)_8]^{4+}$ is closer to a triangular dodecahedral (CShM = 0.91) than to a square-antiprismatic (CShM = 1.24) structure.

$[W(CNMe)_8][AsF_6]_5 \cdot 5$ SO_2 crystallizes in the orthorhombic space group *Pnma*. The structure of the $[W(CNMe)_8]^{5+}$ pentacation is well resolved, as are the $[AsF_6]^-$ counterions, although some displacement ellipsoids of a few fluorine atoms are a little broadened. The SO_2 molecules (solvent) are disordered, however. The W-C bond lengths vary between 2.153(7) Å and 2.169(10) Å and therefore seem to be marginally longer than in the corresponding tetracation, although the difference is relatively small, especially when compared to the experimental uncertainties. The C≡N bond lengths are remarkably short. They differ between 1.113(10) Å and 1.129(14) Å. N-Me bond lengths (1.425(10)-1.452(14) Å) are not significantly different from those in the W(IV) compounds. The coordination geometry of tungsten is best described as a mixed form between a biaugmented trigonal prism (CShM = 1.00), square antiprism (CShM = 1.10) and triangular dodecahedron (CShM = 1.69). Most of the positively polarized methyl protons are involved in hydrogen bonding to fluorine atoms from neighboring $[AsF_6]^-$ molecules (distances 2.3-2.7 Å). Similar H···F contact distances of methyl groups have been observed before, for example between the methyl groups of the highly electrophilic decamethylferrocene dication and hexafluorometalate anions.[31] In all three structures, the C≡N-Me ligands are essentially linear.

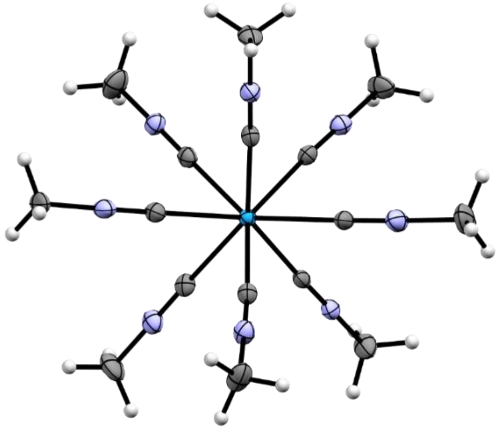


Figure 1. Molecular structure of the complex cation in $[W(CNMe)_8][AsF_6]_4 \cdot 3$ MeCN (ellipsoids drawn at 50% probability).

Computational Studies and Vibrational Spectroscopy

To prove the influence of the oxidation state on C≡N-stretching vibrations and bond lengths, a comparison of literature-known alkyl isocyanide complexes $[W(CNR)_6]$ and $[W(CNR)_7]^{2+}$ with our new species $[W(CNR)_8]^{4+}$ and $[W(CNR)_8]^{5+}$ seemed straightforward. Unfortunately, only a few of such low-valent compounds exist at all and in some cases spectroscopic data are incomplete. Even if molybdenum is also considered, there is no series in which complexes exist for both oxidation states and contain the same alkyl substituent. Furthermore, no crystal structure of a W(0) hexakis(alkylisocyanide) complex exists, while for W(II) only $[W(CNtBu)_7]^{2+}$ has been structurally characterized.[7-8] Therefore, we decided to use DFT calculations (M06L/Def2-TZVP) to compare the structures and vibrational spectra of $[W(CNMe)_6]$, $[W(CNMe)_7]^{2+}$, $[W(CNMe)_8]^{4+}$ and $[W(CNMe)_8]^{5+}$ (Table 1). The resulting calculated $\tilde{\nu}(C{\equiv}N)$ vibrational frequencies of $[W(CNMe)_8]^{4+/5+}$ are well in line with the experimental values while the values of the C-H vibrations show larger deviations from the calculations (Figure 2). This is probably a consequence of strong hydrogen bonding to the anions in the solid state. Trends in W-C and C≡N bond lengths in the crystal structures are also sufficiently well reproduced. Minor discrepancies may result from the comparison of isolated tetra-/pentacations in the gas phase (calculation) with experimental values in the solid state, where significant intermolecular interactions between cations and anions are present.

Table 1: Comparison of W-C and C≡N bond lengths as well as $\tilde{\nu}$(C≡N); calculated values in regular typography, experimental values below *in italics*.

	W-C in Å	**C≡N in Å**	**$\tilde{\nu}$(C≡N) in cm^{-1} (IR)**	**$\tilde{\nu}$(C≡N) in cm^{-1} (Raman)**
$[\mathrm{W(CNMe)_6}]$	2.089	1.184	2089	2096, 2205
$[\mathrm{W(CNMe)_7}]^{2+}$	2.087-2.182	1.161-1.165	2216, 2229, 2236	2216, 2236, 2284
$[\mathrm{W(CNMe)_8}]^{4+}$	2.200	1.154	2281, 2296	2292, 2308
	2.139(5)-2.163(5)	*1.136(7)-1.144(7)*	*2276*	*2289, 2305*
$[\mathrm{W(CNMe)_8}]^{5+}$	2.218	1.153	2280, 2283	2285
	2.153(7)-2.169(10)	*1.113(10)-1.129(14)*	*2284*	*2307*

In general, W-C bond lengths get longer upon oxidation, since fewer and fewer electrons remain in bonding orbitals. In contrast, C≡N bonds get shorter upon oxidation (and consequently, $\tilde{\nu}$(C≡N) increases). This can be explained by the decreased tendency for π-backbonding in case of higher oxidation state metal centers. Additionally, the electrostatic interaction between the lone pair of the isocyanide and the metal center further increases the C≡N bond strength. This is reflected by the fact that especially the high-valent complexes have higher $\tilde{\nu}$(C≡N) than free MeNC itself (IR 2166 cm^{-1}/Raman 2165 cm^{-1})[32] and also slightly shortened C≡N bond lengths (1.167 Å in MeNC).[33] Surprisingly, calculations predict that $\tilde{\nu}$(C≡N) of $[\mathrm{W(CNMe)_8}]^{5+}$ are slightly lower than in $[\mathrm{W(CNMe)_8}]^{4+}$, while this is not the case for the experimentally obtained values. However, the differences in absolute numbers are very small. Differences in experimental W-C and C≡N bond lengths between the W(IV) and W(V) species are marginal and must be treated with care due to the significant standard uncertainties of the bond lengths. In comparison, [W(CN^{t}Bu)$_7$][PF$_6$]$_2$ has significantly shorter W-C bonds (2.069(6)-2.142(8) Å) than [W(CNMe)$_8$]$^{4+/5+}$, while C≡N bond lengths (1.140(7)-1.148(9) Å) are relatively similar.[8] If compared with homoleptic carbonyl complexes where $\tilde{\nu}$(CO) differ by hundreds of wavenumbers in dependence on the oxidation state of the metal,[34] this effect seems to be less pronounced for homoleptic alkyl isocyanide complexes due to their weaker π-acceptor properties.[35]

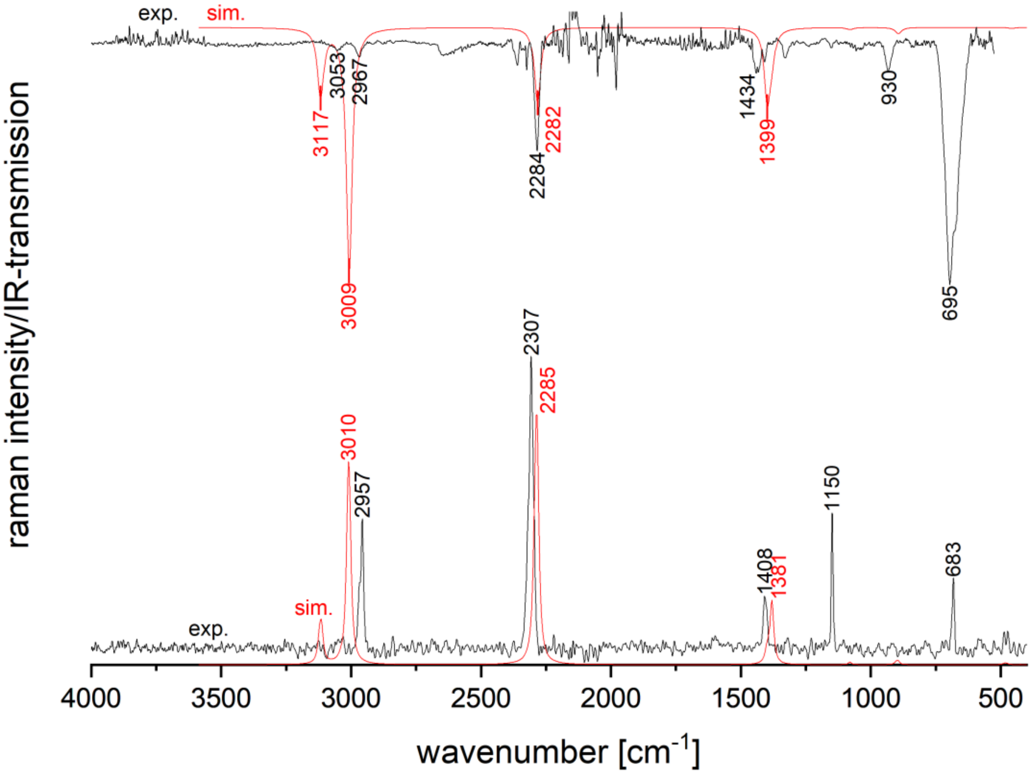


Figure 2. Experimental IR (up) and Raman spectra (down) of [W(CNMe)$_8$][AsF$_6$]$_5$·5 SO$_2$ (black lines). Simulated IR and Raman spectra of [W(CNMe)$_8$]$^{5+}$ (red lines).

NMR Spectroscopy

Additionally, multinuclear NMR spectroscopy was used to characterize the new W(IV) compounds. Due to the ionic nature of the products, highly polar d_3-acetonitrile had to be used as a solvent. These solutions were sufficiently stable for short times, but degradation of the samples was clearly visible after a few days. ^{1}H NMR spectra of isolated $[W(CNMe)_8][OTf]_4$ displayed one main product ($\delta = 3.85$ ppm), however significant amounts of side products ($\delta = 3.88$ ppm) were present. The existence of at least two species in the mixture was also confirmed via DOSY NMR although the structure of the side product could not be assigned with certainty. ^{13}C chemical shifts were obtained by two-dimensional NMR spectroscopy (HMQC, HMBC). ^{13}C signals for the isocyanide carbon were in the range of 115.3 ppm (major component) and 112.5 ppm (minor component), while only one signal for the methyl group could be observed ($\delta = 31.8$ ppm). The ^{15}N HMQC spectrum revealed one signal at 141 ppm (referenced vs. NH_3) that could be assigned to the isocyanide nitrogen. Although the crystal structure proves that methyl triflate is able to methylate $[W(CN)_8]^{4-}$ eight times, the usefulness of this method is limited to the significant amounts of side products, which cannot be separated from the product.

^{1}H-NMR spectra of $[W(CNMe)_8][AsF_6]_4$ revealed that less side products were present. Furthermore, the chemical shift of the main signal was almost identical to the corresponding triflate salt ($\delta = 3.85$ ppm). ^{13}C NMR chemical shifts of the methyl group ($\delta = 31.8$ ppm) and the isocyanide carbon ($\delta = 115.3$ ppm) were assigned from the ^{13}C HMQC and ^{13}C HMBC spectra. The ^{13}C chemical shift of the isocyanide moiety in $[W(CNMe)_8]^{4+}$ is in excellent agreement with $[W(CNH)_8]^{4+}$ [36] while the ^{15}N NMR shift of $[W(CNMe)_8]^{4+}$ is at relatively high field ($\delta = 141$ ppm). Both the higher ^{15}N and ^{13}C chemical shifts of the free alkyl isocyanide CH_3NC[37] (in comparison with its coordinated form) are in accordance with the literature (Table 2).[38]

Table 1. Comparison of NMR shifts from cyanometalates and isonitrile complexes in ppm. ^{13}C & ^{1}H relative to TMS in $CDCl_3$ and ^{14}N & ^{15}N relative to liquid NH_3.

	$^{14}N/^{15}N$	^{13}C	^{1}H
$[W(CNMe)_8][AsF_6]_4$ in d_3-MeCN	141	115.3	3.85
		31.8 (methyl-C)	
$[Mo(CNMe)_7][PF_6]_2$ in d_6-acetone[5]		154	
		34 (methyl-C)	
MeNC[37]	166	158	2.85
		27 (methyl-C)	
$[W(CNH)_8][SbF_6]_4$ in HF[21]	203	115	
$K_4[W(CN)_8]$ in D_2O[21]	284	143	

EPR Spectroscopy

The $5d^1$ electron configuration of $[W(CNMe)_8][AsF_6]_5$ allows the detection of EPR spectra. Figure 3 shows a solution spectrum recorded at −196 °C in frozen SO_2. It reflects essentially axial symmetry with a considerable degree of isotropy for the *g* values. Couplings of $25 \cdot 10^{-4}$ cm^{-1} and $65 \cdot 10^{-4}$ cm^{-1} are due to the interaction of the unpaired electron with the nuclear spin of ^{183}W (I = ½, natural abundance: 14.3%). General features of the spectrum of $[W(CNMe)_8]^{5+}$ well resemble with the spectral parameters derived for the octacyanotungstate(V) anion (see Supporting Information).[39] The line widths are relatively broad and prevent the resolution of further couplings, particularly such of the ^{13}C nuclei of the ligands. A mainly metal-centered unpaired electron can be concluded from the detected ^{183}W hyperfine couplings. Following the detailed discussions outlined by McGarvey for $[W(CN)_8]^{3-}$ [39a] and having in mind the close relationship between the (almost) axially-symmetric EPR parameters of octacyanotungstate and those of $[W(CNMe)_8]^{5+}$, an essentially antiprismatic structure (D_{4d}) for the latter species seems to be probably present in solution. However, the assignment of a molecular structure of paramagnetic octacyanometalates simply based on EPR spectroscopy is complicated by various factors (e.g. intermediate geometries, influence of solvent and counterions, inadequacy of the crystal field model for highly covalent metal-ligand bonds).[40] As stated before, the pentacation in single crystals of $[W(CNMe)_8][AsF_6]_5\cdot5\,SO_2$ displays an intermediate geometry (between a biaugmented trigonal prism, square antiprism and triangular dodecahedron).

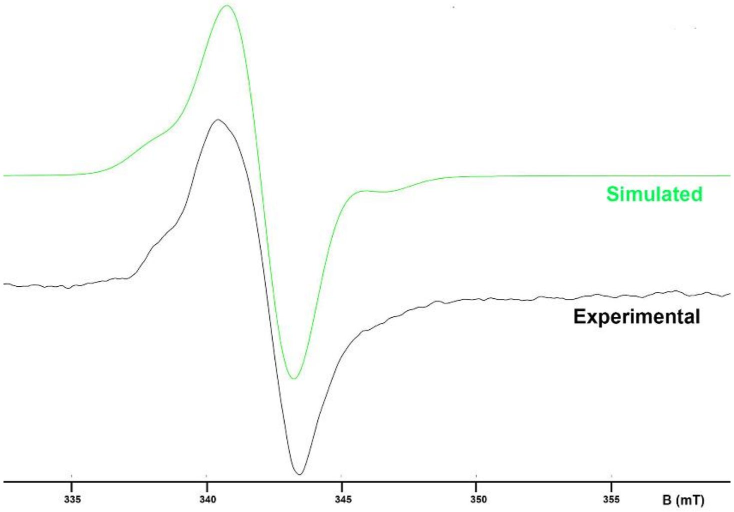


Figure 3. Frozen solution X-band EPR spectrum of $[W(CNMe)_8][AsF_6]_5$ at −196 °C in SO_2.

CONCLUSION

In summary, we report the synthesis and structural characterization of the first homoleptic eight-coordinate isocyanide complexes $[W(CNMe)_8]^{4+}$ and $[W(CNMe)_8]^{5+}$ by reacting octacyanometalates $[W(CN)_8]^{4-/3-}$ with powerful electrophilic methylating agents. Moreover, the tetracation completes the series of 18-electron complexes $[W(CNR)_6]$ and $[W(CNR)_7]^{2+}$. The existence of the tetra- and pentacation demonstrates that even metal ions in high oxidation states can form homoleptic alkyl isocyanide complexes, although they are typically associated to be ligands for low oxidation states.

ASSOCIATED CONTENT

Supporting Information.

Information regarding the X-Ray structures of the single crystals, IR/Raman, NMR, EPR spectroscopy as well as the DFT calculations can be found in the supporting information free of charge.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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