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Synthesis of diaminoacetylene from cyanido ligands of the octacyanidotungstate(IV) complex

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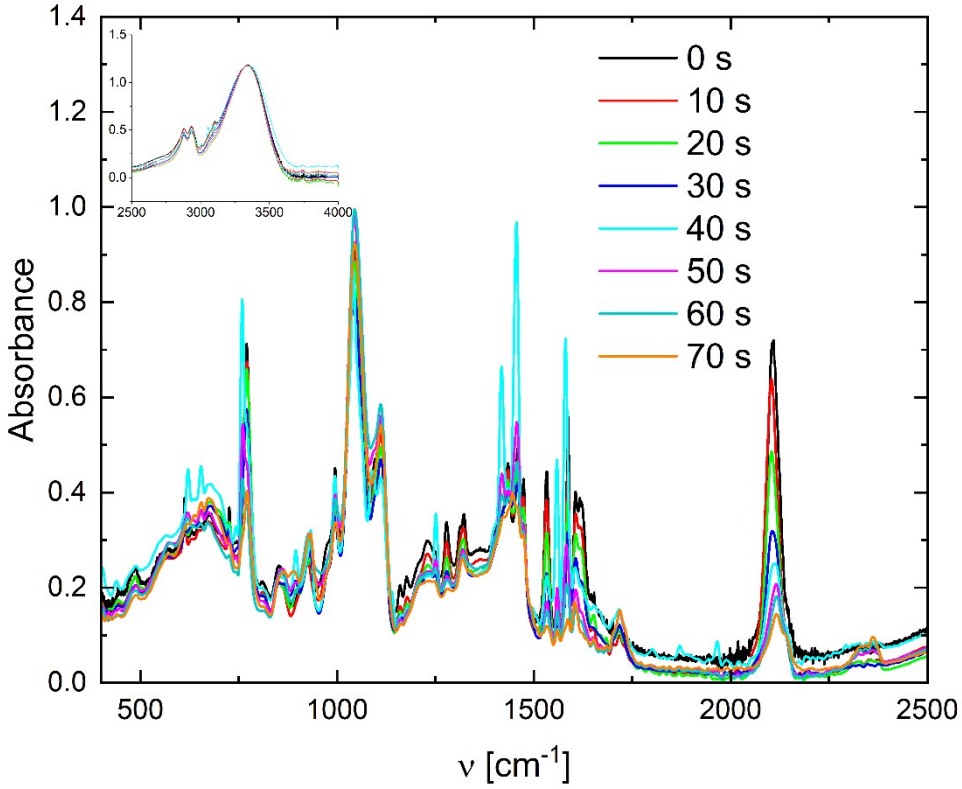

Figure S1. The IR (after ATR correction) spectra of glycerol solution of $(bpyH)_3(H_3O)[W(CN)_8]\cdot H_2O$ (conditions as in synthesis of **1**) T = 22 ˚C. The legend shows the heating time.

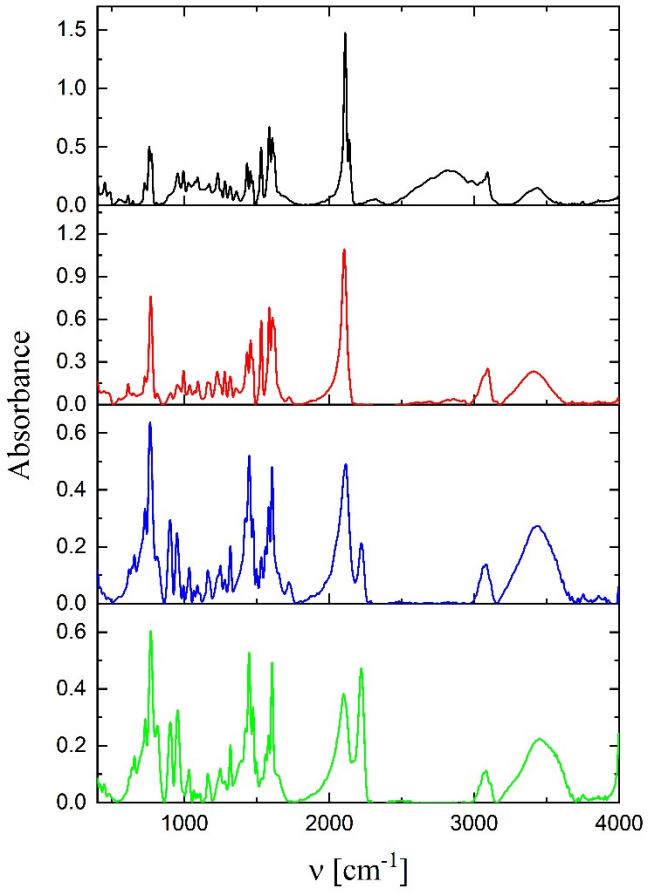

Figure S2. The IR spectra of $(bpyH)_3(H_3O)[W(CN)_8]\cdot H_2O$ decomposed in solid state. T = 295.15 K. Black line - spectrum of $(bpyH)_3(H_3O)[W(CN)_8]\cdot H_2O$, red line - spectrum recorded after 5s of heating, blue line - spectrum recorded after 20 s of heating and green line - spectrum recorded after 40 s of heating.

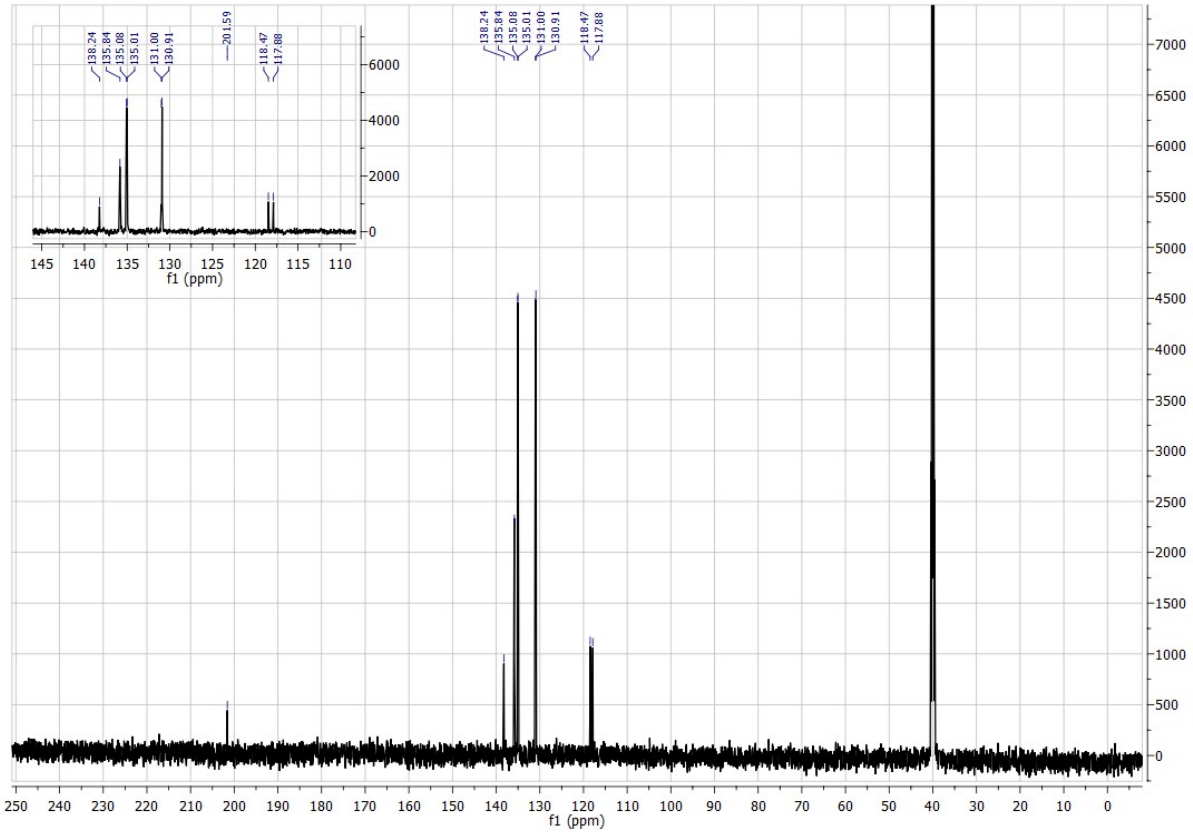

Figure S3. ^{13}C-NMR spectrum of **1**. (DMSO-d_6) σ [ppm] = 201.59 (C≡C), 138.24 (Ar), 135.84 (Ar), 135.08 (Ar), 135.01 (Ar), 131.00 (Ar), 130.91 (Ar), 118.47 (C≡N), 117.88 (C≡N).

Table S1. Crystal data and structure refinement for **1-3**.

		1	**2**	**3**
Empirical formula		$C_{56}H_{50}N_8O_2P_2W$	$C_8H_8N_8O_2Rb_2W$	$C_{16}H_{10}Cs_4N_{16}OW_2$
Formula moiety		$(PPh_4^+)_2$, $[W(CN)_6(C_2N_2H_4)]^{2-}$, $2(H_2O)$	$(Rb^+)_2$, $[W(CN)_6(C_2N_2H_4)]^{2-}$, $2(H_2O)$	$(Cs^+)_2$, $[W(CN)_6(C_2N_2H_4)]^{2-}$, $0.5(H_2O)$
Formula weight		1108.80	601.00	1331.66
Temperature [K]		260(2)	293(2)	100(2)
Wavelength [Å]		1.54184	0.71073	0.71073
Crystal system		Triclinic	Monoclinic	Monoclinic
Space group		$P\bar{1}$	P $2_1/c$	P c
Unit cell dimensions	a [Å]	12.61380(10)	8.5484(2)	11.8245(3)
	b [Å]	21.62890(10)	14.3462(3)	8.6678(2)
	c [Å]	21.86200(10)	12.8770(2)	14.9294(4)
	α [°]	117.8730(10)	90	90
	β [°]	90.93	90.846(2)	98.581(2)
	γ [°]	103.30	90	90
Volume [Å^3]		5077.68(7)	1579.03(6)	1513.02(7)
Z		4	4	2
Density (calculated) [g/cm^3]		1.450	2.528	2.923
Absorption coefficient [mm^{-1}]		5.208	13.456	12.379
F(000)		2232	1096	1168
Crystal size [mm^3]		0.300 x 0.200 x 0.100	0.200 × 0.200 × 0.100	0.300 x 0.100 x 0.020
Theta range for data collection [°]		3.782 to 76.783	3.469 to 31.476	3.344 to 30.856
Index ranges		$-15 \le h \le 15$ $-26 \le k \le 26$ $-27 \le l \le 26$	$-11 \le h \le 12$ $-19 \le k \le 20$ $-17 \le l \le 18$	$-16 \le h \le 16$ $-12 \le k \le 10$ $-19 \le l \le 20$
Reflections collected		151357	43334	27955
Independent reflections		20086 [R(int) = 0.0796]	4682 [R(int) = 0.0474]	7379 [R(int) = 0.0589]
Completeness to theta [%]		99.7	99.6	99.7
Refinement method		Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters		20086 / 6 / 1292	4682 / 2 / 215	7379 / 2 / 347
Goodness-of-fit on F2		1.062	1.072	1.010
Final R indices [I>2σ(I)]		R1 = 0.0379, wR2 = 0.1043	R1 = 0.0233, wR2 = 0.0476	R1 = 0.0348, wR2 = 0.0837
R indices (all data)		R1 = 0.0415, wR2 = 0.1072	R1 = 0.0304, wR2 = 0.0491	R1 = 0.0359, wR2 = 0.0846
Largest diff. peak and hole [e/Å^3]		1.227 and -1.887	2.223 and -1.991	1.622 and -2.067

Table S2. Selected bond parameters of **1**-**3**.

1		**2**		**3**	
Bond lengths [Å]					
W(1)-C(2)	2.040(3)	W(1)-C(1)	2.015(7)	W(1)-C(10)	2.033(10)
W(1)-C(1)	2.048(3)	W(1)-C(2)	2.056(8)	W(1)-C(9)	2.066(11)
W(1)-C(8)	2.170(3)	W(1)-C(7)	2.167(7)	W(1)-C(14)	2.158(10)
W(1)-C(5)	2.178(3)	W(1)-C(6)	2.170(7)	W(1)-C(16)	2.162(11)
W(1)-C(6)	2.184(3)	W(1)-C(5)	2.174(7)	W(1)-C(11)	2.174(11)
W(1)-C(3)	2.184(3)	W(1)-C(8)	2.179(7)	W(1)-C(15)	2.182(12)
W(1)-C(7)	2.187(3)	W(1)-C(3)	2.202(5)	W(1)-C(13)	2.193(12)
W(1)-C(4)	2.250(3)	W(1)-C(4)	2.230(8)	W(1)-C(12)	2.234(11)
W(2)-C(10)	2.044(3)	W(2)-C(9)	2.038(7)	W(2)-C(1)	2.034(10)
W(2)-C(9)	2.049(3)	W(2)-C(10)	2.053(8)	W(2)-C(2)	2.060(11)
W(2)-C(16)	2.175(3)	W(2)-C(16)	2.162(7)	W(2)-C(7)	2.164(10)
W(2)-C(15)	2.178(3)	W(2)-C(13)	2.172(7)	W(2)-C(8)	2.166(11)
W(2)-C(13)	2.179(3)	W(2)-C(14)#1	2.180(8)	W(2)-C(6)	2.167(11)
W(2)-C(11)	2.179(3)	W(2)-C(15)	2.184(7)	W(2)-C(5)	2.171(11)
W(2)-C(14)	2.182(3)	W(2)-C(11)#2	2.189(6)	W(2)-C(3)	2.190(12)
W(2)-C(12)	2.251(4)	W(2)-C(12)#2	2.227(8)	W(2)-C(4)	2.220(10)
Angles [°]					
C(2)-W(1)-C(1)	39.15(12)	C(1)-W(1)-C(2)	39.5(2)	C(10)-W(1)-C(9)	39.1(4)
C(2)-W(1)-C(8)	97.28(13)	C(1)-W(1)-C(7)	79.9(3)	C(10)-W(1)-C(14)	80.3(4)
C(1)-W(1)-C(8)	92.99(12)	C(2)-W(1)-C(7)	109.2(3)	C(9)-W(1)-C(14)	114.4(4)
C(2)-W(1)-C(5)	117.39(12)	C(1)-W(1)-C(6)	99.8(3)	C(10)-W(1)-C(16)	101.7(4)
C(1)-W(1)-C(5)	78.91(12)	C(2)-W(1)-C(6)	84.6(3)	C(9)-W(1)-C(16)	86.1(4)
C(8)-W(1)-C(5)	72.73(12)	C(7)-W(1)-C(6)	71.1(2)	C(14)-W(1)-C(16)	141.0(4)
C(2)-W(1)-C(6)	83.67(13)	C(1)-W(1)-C(5)	82.2(3)	C(10)-W(1)-C(11)	80.8(4)
C(1)-W(1)-C(6)	110.07(12)	C(2)-W(1)-C(5)	115.6(3)	C(9)-W(1)-C(11)	109.1(4)
C(8)-W(1)-C(6)	141.40(12)	C(7)-W(1)-C(5)	72.8(3)	C(14)-W(1)-C(11)	71.2(4)
C(5)-W(1)-C(6)	140.35(12)	C(6)-W(1)-C(5)	142.9(3)	C(16)-W(1)-C(11)	70.8(4)
C(2)-W(1)-C(3)	76.10(13)	C(1)-W(1)-C(8)	95.6(3)	C(10)-W(1)-C(15)	97.5(4)
C(1)-W(1)-C(3)	111.50(13)	C(2)-W(1)-C(8)	85.5(3)	C(9)-W(1)-C(15)	89.9(4)
C(8)-W(1)-C(3)	71.31(12)	C(7)-W(1)-C(8)	146.5(2)	C(14)-W(1)-C(15)	72.5(4)
C(5)-W(1)-C(3)	142.94(13)	C(6)-W(1)-C(8)	141.8(2)	C(16)-W(1)-C(15)	143.6(4)
C(6)-W(1)-C(3)	71.53(13)	C(5)-W(1)-C(8)	73.7(3)	C(11)-W(1)-C(15)	143.4(4)
C(2)-W(1)-C(7)	102.06(13)	C(1)-W(1)-C(3)	123.5(3)	C(10)-W(1)-C(13)	124.3(4)

C(1)-W(1)-C(7)	83.50(12)	C(2)-W(1)-C(3)	84.1(3)	C(9)-W(1)-C(13)	85.4(4)
C(8)-W(1)-C(7)	143.87(12)	C(7)-W(1)-C(3)	138.7(3)	C(14)-W(1)-C(13)	139.0(4)
C(5)-W(1)-C(7)	71.31(12)	C(6)-W(1)-C(3)	71.5(3)	C(16)-W(1)-C(13)	71.5(4)
C(6)-W(1)-C(7)	71.56(12)	C(5)-W(1)-C(3)	137.5(3)	C(11)-W(1)-C(13)	138.2(4)
C(3)-W(1)-C(7)	143.02(12)	C(8)-W(1)-C(3)	70.8(3)	C(15)-W(1)-C(13)	72.1(4)
C(2)-W(1)-C(4)	160.35(13)	C(1)-W(1)-C(4)	156.2(2)	C(10)-W(1)-C(12)	156.7(4)
C(1)-W(1)-C(4)	160.50(13)	C(2)-W(1)-C(4)	163.3(2)	C(9)-W(1)-C(12)	163.8(4)
C(8)-W(1)-C(4)	85.07(12)	C(7)-W(1)-C(4)	79.7(3)	C(14)-W(1)-C(12)	80.7(4)
C(5)-W(1)-C(4)	82.00(12)	C(6)-W(1)-C(4)	85.0(3)	C(16)-W(1)-C(12)	84.8(4)
C(6)-W(1)-C(4)	82.47(12)	C(5)-W(1)-C(4)	80.2(2)	C(11)-W(1)-C(12)	80.4(4)
C(3)-W(1)-C(4)	86.31(13)	C(8)-W(1)-C(4)	94.7(3)	C(15)-W(1)-C(12)	89.5(4)
C(7)-W(1)-C(4)	86.67(13)	C(3)-W(1)-C(4)	80.1(2)	C(13)-W(1)-C(12)	79.0(4)

Table S3. Intermetallic distances in **2** and **3** [Å].

2		
W1		
	4.5802(5)	Rb1 [-x,1/2+y,1/2-z]
	4.9206(5)	Rb2 [-1+x,1/2-y,-1/2+z]
Rb1		
	4.3730(6)	Rb2
	4.5802(5)	W1 [-x,-1/2+y,1/2-z]
	4.8712(7)	Rb2 [1-x,-y,1-z]
	4.9599(6)	Rb2 [x,1/2-y,-1/2+z]
Rb2		
	4.3730(6)	Rb1
	4.8712(7)	Rb1 [1-x,-y,1-z]
	4.9206(5)	W1 [1+x,1/2-y,1/2+z]
	4.9599(6)	Rb1 [x,1/2-y,1/2+z]
3		
W1		
	4.6614(1)	Cs4 [-1+x,y,z]
	4.7074(1)	Cs2 [x,1-y,-1/2+z]
W2		
	4.6127(1)	Cs3
	4.6673(1)	Cs1 [1+x,1-y,-1/2+z]
Cs1		
	4.5788(1)	Cs2 [x,1-y,1/2+z]
	4.7753(1)	Cs2 [x,1+y,z]
	4.7970(1)	Cs4 [-1+x,y,z]
Cs2		
	4.5510(1)	Cs3 [-1+x,y,z]
Cs3		
	4.8652(1)	Cs4 [x,1-y,1/2+z]