

Supplementary Information

Unusual structure changes going from Li⁺ to Cs⁺ in [W(CN)₆(bpy)]²⁻ ion salts. The Na⁺ case.

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Table S1. Bond lengths [Å] and angles [°] for **1** and **2**.

1				2			
Bond length		Angle		Bond length		Angle	
W(1)-C(15)	2.143(5)	C(15)-W(1)-C(16)	69.77(18)	W(1)-C(14)	2.144(5)	C(14)-W(1)-C(13)	71.2(2)
W(1)-C(16)	2.157(5)	C(15)-W(1)-C(14)	71.23(18)	W(1)-C(13)	2.144(6)	C(14)-W(1)-C(15)	112.7(2)
W(1)-C(14)	2.159(5)	C(16)-W(1)-C(14)	111.02(18)	W(1)-C(15)	2.153(6)	C(13)-W(1)-C(15)	69.2(3)
W(1)-C(13)	2.164(5)	C(15)-W(1)-C(13)	74.06(19)	W(1)-C(16)	2.156(5)	C(14)-W(1)-C(16)	72.16(18)
W(1)-C(18)#1	2.166(5)	C(16)-W(1)-C(13)	137.37(19)	W(1)-C(12)	2.158(5)	C(13)-W(1)-C(16)	111.4(3)
W(1)-C(17)	2.172(5)	C(14)-W(1)-C(13)	76.71(18)	W(1)-C(11)	2.161(6)	C(15)-W(1)-C(16)	74.7(2)
W(1)-N(1)	2.215(4)	C(15)-W(1)-C(18)#1	77.38(18)	W(1)-N(1)	2.216(4)	C(14)-W(1)-C(12)	139.78(18)
W(1)-N(12)	2.227(4)	C(16)-W(1)-C(18)#1	78.99(18)	W(1)-N(2)	2.234(4)	C(13)-W(1)-C(12)	78.6(2)

W(2)-C(36)	2.135(5)	C(14)-W(1)-C(18)#1	140.28(19)	Na(1)-O(1A)	1.980(9)	C(15)-W(1)-C(12)	79.02(19)
W(2)-C(37)	2.153(6)	C(13)-W(1)-C(18)#1	71.66(18)	Na(1)-O(2)	2.091(9)	C(16)-W(1)-C(12)	145.64(18)
W(2)-C(35)	2.155(5)	C(15)-W(1)-C(17)	112.13(19)	Na(1)-N(7)	2.302(9)	C(14)-W(1)-C(11)	76.10(19)
W(2)-C(34)	2.163(5)	C(16)-W(1)-C(17)	74.13(18)	Na(1)-N(3)#1	2.333(8)	C(13)-W(1)-C(11)	74.6(3)
W(2)-C(38)	2.164(5)	C(14)-W(1)-C(17)	71.18(17)	Na(1)-O(1B)	2.348(10)	C(15)-W(1)-C(11)	136.5(3)
W(2)-C(33)	2.167(5)	C(13)-W(1)-C(17)	142.40(17)	Na(1)-O(1A)#2	2.386(9)	C(16)-W(1)-C(11)	143.1(2)
W(2)-N(32)	2.208(4)	C(18)#1-W(1)-C(17)	145.45(18)	Na(1)-C(15)	3.047(8)	C(12)-W(1)-C(11)	70.7(2)
W(2)-N(21)	2.233(4)	C(15)-W(1)-N(1)	142.92(16)	Na(1)-Na(2)	3.542(5)	C(14)-W(1)-N(1)	80.87(16)
Na(1)-N(18)	2.398(5)	C(16)-W(1)-N(1)	145.81(17)	Na(1)-Na(1)#2	3.644(9)	C(13)-W(1)-N(1)	144.0(2)
Na(1)-O(2)	2.429(4)	C(14)-W(1)-N(1)	81.59(16)	Na(2)-N(5B)	2.349(14)	C(15)-W(1)-N(1)	145.0(2)
Na(1)-O(1)	2.508(4)	C(13)-W(1)-N(1)	75.51(17)	Na(2)-O(3)	2.413(7)	C(16)-W(1)-N(1)	79.76(18)
Na(1)-N(15)	2.515(5)	C(18)#1-W(1)-N(1)	112.18(17)	Na(2)-O(1A)#2	2.418(7)	C(12)-W(1)-N(1)	112.14(16)
Na(1)-N(38)	2.523(4)	C(17)-W(1)-N(1)	80.87(17)	Na(2)-N(4)#3	2.447(5)	C(11)-W(1)-N(1)	77.0(2)
Na(1)-O(7)	2.714(4)	C(15)-W(1)-N(12)	142.71(16)	Na(2)-O(2)	2.460(6)	C(14)-W(1)-N(2)	142.98(17)
Na(1)-Na(2)	3.805(3)	C(16)-W(1)-N(12)	80.68(16)	Na(2)-N(6)#4	2.469(5)	C(13)-W(1)-N(2)	142.4(2)
Na(3)-O(7)	2.347(4)	C(14)-W(1)-N(12)	143.19(17)	Na(2)-N(5A)	2.69(2)	C(15)-W(1)-N(2)	79.5(2)
Na(3)-O(9)	2.347(4)	C(13)-W(1)-N(12)	119.02(17)	Na(2)-O(1B)#2	2.787(10)	C(16)-W(1)-N(2)	78.33(18)

Na(3)-O(8)	2.378(4)	C(18)#1-W(1)-N(12)	75.01(17)	O(1B)-O(5)	1.572(13)	C(12)-W(1)-N(2)	75.41(17)
Na(3)-N(35)#2	2.451(5)	C(17)-W(1)-N(12)	79.52(16)			C(11)-W(1)-N(2)	120.14(19)
Na(3)-N(13)#1	2.481(5)	N(1)-W(1)-N(12)	72.02(14)			N(1)-W(1)-N(2)	72.19(15)
Na(3)-Na(4)#2	3.527(3)	C(36)-W(2)-C(37)	75.6(2)			O(1A)-Na(1)-O(2)	139.7(4)
Na(2)-O(6)	2.321(4)	C(36)-W(2)-C(35)	68.12(19)			O(1A)-Na(1)-N(7)	91.0(3)
Na(2)-O(3)	2.347(4)	C(37)-W(2)-C(35)	135.4(2)			O(2)-Na(1)-N(7)	120.3(3)
Na(2)-O(1)	2.374(4)	C(36)-W(2)-C(34)	79.90(18)			O(1A)-Na(1)-N(3)#1	106.7(3)
Na(2)-O(5)	2.440(4)	C(37)-W(2)-C(34)	69.49(17)			O(2)-Na(1)-N(3)#1	96.9(3)
Na(2)-O(4)	2.519(5)	C(35)-W(2)-C(34)	79.17(18)			N(7)-Na(1)-N(3)#1	92.9(3)
Na(2)-O(2)	2.625(5)	C(36)-W(2)-C(38)	71.17(18)			O(2)-Na(1)-O(1B)	119.3(4)
Na(4)-O(8)#3	2.391(4)	C(37)-W(2)-C(38)	75.65(19)			N(7)-Na(1)-O(1B)	119.7(3)
Na(4)-O(10)	2.430(5)	C(35)-W(2)-C(38)	114.10(19)			N(3)#1-Na(1)-O(1B)	88.2(3)
Na(4)-N(14)	2.437(4)	C(34)-W(2)-C(38)	139.1(2)			O(1A)-Na(1)-O(1A)#2	67.2(3)
Na(4)-O(9)#3	2.450(4)	C(36)-W(2)-C(33)	110.05(19)			O(2)-Na(1)-O(1A)#2	83.6(3)
Na(4)-N(36)	2.493(5)	C(37)-W(2)-C(33)	143.83(17)			N(7)-Na(1)-O(1A)#2	96.5(3)
Na(4)-N(34)#4	2.528(5)	C(35)-W(2)-C(33)	75.23(18)			N(3)#1-Na(1)-O(1A)#2	168.8(4)
N(13)-C(13)	1.141(6)	C(34)-W(2)-C(33)	146.01(17)			O(1A)-Na(1)-C(15)	108.6(3)

N(15)-C(15)	1.156(7)	C(38)-W(2)-C(33)	73.00(19)			O(2)-Na(1)-C(15)	101.5(3)
N(38)-C(38)	1.152(6)	C(36)-W(2)-N(32)	145.42(16)			N(7)-Na(1)-C(15)	18.9(2)
N(32)-C(27)	1.363(6)	C(37)-W(2)-N(32)	78.60(18)			N(3)#1-Na(1)-C(15)	94.0(3)
N(32)-C(31)	1.367(6)	C(35)-W(2)-N(32)	144.28(18)			O(1B)-Na(1)-C(15)	138.6(3)
N(21)-C(26)	1.353(6)	C(34)-W(2)-N(32)	111.93(16)			O(1A)#2-Na(1)-C(15)	96.9(3)
N(21)-C(22)	1.356(6)	C(38)-W(2)-N(32)	80.44(17)			O(1A)-Na(1)-Na(2)	109.0(3)
N(34)-C(34)	1.153(6)	C(33)-W(2)-N(32)	78.83(17)			O(2)-Na(1)-Na(2)	42.82(17)
N(35)-C(35)	1.147(6)	C(36)-W(2)-N(21)	141.89(16)			N(7)-Na(1)-Na(2)	104.6(2)
N(36)-C(36)	1.159(7)	C(37)-W(2)-N(21)	120.68(17)			N(3)#1-Na(1)-Na(2)	139.6(2)
N(37)-C(37)	1.160(7)	C(35)-W(2)-N(21)	78.84(17)			O(1B)-Na(1)-Na(2)	112.5(3)
N(33)-C(33)	1.146(6)	C(34)-W(2)-N(21)	75.63(16)			O(1A)#2-Na(1)-Na(2)	42.84(19)
N(14)-C(14)	1.146(6)	C(38)-W(2)-N(21)	142.98(18)			C(15)-Na(1)-Na(2)	92.00(18)
N(16)-C(16)	1.146(6)	C(33)-W(2)-N(21)	77.77(16)			O(1A)-Na(1)-Na(1)#2	37.1(2)
N(17)-C(17)	1.148(6)	N(32)-W(2)-N(21)	71.94(15)			O(2)-Na(1)-Na(1)#2	110.0(3)
N(18)-C(18)	1.131(6)	N(18)-Na(1)-O(2)	91.50(16)			N(7)-Na(1)-Na(1)#2	94.9(2)
		N(18)-Na(1)-O(1)	157.81(15)			N(3)#1-Na(1)-Na(1)#2	143.0(3)
		O(2)-Na(1)-O(1)	80.12(15)			O(1A)#2-Na(1)-Na(1)#2	30.05(19)

		N(18)-Na(1)-N(15)	96.36(16)			C(15)-Na(1)-Na(1)#2	104.6(2)
		O(2)-Na(1)-N(15)	165.48(18)			Na(2)-Na(1)-Na(1)#2	72.38(13)
		O(1)-Na(1)-N(15)	88.13(15)			N(5B)-Na(2)-O(3)	158.6(8)
		N(18)-Na(1)-N(38)	103.17(16)			O(3)-Na(2)-O(1A)#2	76.7(3)
		O(2)-Na(1)-N(38)	99.81(15)			N(5B)-Na(2)-N(4)#3	99.9(5)
		O(1)-Na(1)-N(38)	98.52(14)			O(3)-Na(2)-N(4)#3	92.54(19)
		N(15)-Na(1)-N(38)	90.29(15)			O(1A)#2-Na(2)-N(4)#3	89.6(2)
		N(18)-Na(1)-O(7)	75.30(14)			N(5B)-Na(2)-O(2)	79.4(7)
		O(2)-Na(1)-O(7)	93.60(14)			O(3)-Na(2)-O(2)	84.2(2)
		O(1)-Na(1)-O(7)	84.70(13)			O(1A)#2-Na(2)-O(2)	75.6(2)
		N(15)-Na(1)-O(7)	76.72(13)			N(4)#3-Na(2)-O(2)	165.2(2)
		N(38)-Na(1)-O(7)	166.55(16)			O(3)-Na(2)-N(6)#4	99.7(2)
		N(18)-Na(1)-Na(2)	133.25(14)			O(1A)#2-Na(2)-N(6)#4	171.9(2)
		O(2)-Na(1)-Na(2)	43.14(11)			N(4)#3-Na(2)-N(6)#4	97.91(18)
		O(1)-Na(1)-Na(2)	37.54(10)			O(2)-Na(2)-N(6)#4	96.8(2)
		N(15)-Na(1)-Na(2)	125.67(13)			O(3)-Na(2)-N(5A)	172.1(5)
		N(38)-Na(1)-Na(2)	96.72(12)			N(4)#3-Na(2)-N(5A)	90.2(4)

		O(7)-Na(1)-Na(2)	93.74(10)			O(2)-Na(2)-N(5A)	91.3(5)
		O(7)-Na(3)-O(9)	117.89(18)			N(6)#4-Na(2)-N(5A)	87.3(4)
		O(7)-Na(3)-O(8)	82.77(15)			O(3)-Na(2)-O(1B)#2	100.2(2)
		O(9)-Na(3)-O(8)	84.06(14)			O(1A)#2-Na(2)-O(1B)#2	27.3(3)
		O(7)-Na(3)-N(35)#2	115.80(16)			N(4)#3-Na(2)-O(1B)#2	74.9(2)
		O(9)-Na(3)-N(35)#2	126.23(17)			O(2)-Na(2)-O(1B)#2	91.5(3)
		O(8)-Na(3)-N(35)#2	100.04(16)			N(6)#4-Na(2)-O(1B)#2	159.0(2)
		O(7)-Na(3)-N(13)#1	92.17(16)			N(5B)-Na(2)-Na(1)	71.5(7)
		O(9)-Na(3)-N(13)#1	95.91(15)			O(3)-Na(2)-Na(1)	87.2(2)
		O(8)-Na(3)-N(13)#1	174.22(17)			O(1A)#2-Na(2)-Na(1)	42.15(19)
		N(35)#2-Na(3)-N(13)#1	84.66(16)			N(4)#3-Na(2)-Na(1)	130.34(15)
		O(7)-Na(3)-Na(4)#2	112.44(13)			O(2)-Na(2)-Na(1)	35.3(2)
		O(9)-Na(3)-Na(4)#2	43.81(10)			N(6)#4-Na(2)-Na(1)	131.10(15)
		O(8)-Na(3)-Na(4)#2	42.44(9)			N(5A)-Na(2)-Na(1)	85.4(5)
		N(35)#2-Na(3)-Na(4)#2	110.73(13)			O(1B)#2-Na(2)-Na(1)	56.5(2)
		N(13)#1-Na(3)-Na(4)#2	138.85(12)			Na(1)-O(1A)-Na(1)#2	112.8(3)
		O(6)-Na(2)-O(3)	154.00(18)			Na(1)-O(1A)-Na(2)#2	149.5(4)

		O(6)-Na(2)-O(1)	98.17(15)			Na(1)#2-O(1A)-Na(2)#2	95.0(3)
		O(3)-Na(2)-O(1)	107.45(15)			O(5)-O(1B)-Na(1)	104.7(5)
		O(6)-Na(2)-O(5)	86.87(15)			O(5)-O(1B)-Na(2)#2	143.8(5)
		O(3)-Na(2)-O(5)	86.19(15)			Na(1)-O(1B)-Na(2)#2	111.2(4)
		O(1)-Na(2)-O(5)	115.30(17)			Na(1)-O(2)-Na(2)	101.9(3)
		O(6)-Na(2)-O(4)	73.55(15)			C(14)-N(6)-Na(2)#4	162.9(4)
		O(3)-Na(2)-O(4)	81.53(15)			C(15)-N(7)-Na(1)	120.5(6)
		O(1)-Na(2)-O(4)	152.41(18)			C(11)-N(3)-Na(1)#5	137.9(7)
		O(5)-Na(2)-O(4)	90.90(15)			C(12)-N(4)-Na(2)#3	151.6(4)
		O(6)-Na(2)-O(2)	80.08(15)			N(4)-C(12)-W(1)	178.2(5)
		O(3)-Na(2)-O(2)	100.30(15)			N(6)-C(14)-W(1)	177.8(4)
		O(1)-Na(2)-O(2)	78.76(14)			N(8)-C(16)-W(1)	176.3(5)
		O(5)-Na(2)-O(2)	162.23(16)			N(7)-C(15)-W(1)	177.3(5)
		O(4)-Na(2)-O(2)	73.93(15)			N(7)-C(15)-Na(1)	40.6(5)
		O(6)-Na(2)-Na(1)	83.81(12)			W(1)-C(15)-Na(1)	140.8(3)
		O(3)-Na(2)-Na(1)	113.09(12)			N(3)-C(11)-W(1)	175.8(6)
		O(1)-Na(2)-Na(1)	40.07(11)			N(5B)-C(13)-W(1)	164.2(17)

		O(5)-Na(2)-Na(1)	151.13(12)			N(5A)-C(13)-W(1)	161.8(14)
		O(4)-Na(2)-Na(1)	112.34(13)			C(13)-N(5A)-Na(2)	123.0(18)
		O(2)-Na(2)-Na(1)	39.24(10)			C(13)-N(5B)-Na(2)	169(2)
		O(8)#3-Na(4)-O(10)	83.50(14)				
		O(8)#3-Na(4)-N(14)	175.27(18)				
		O(10)-Na(4)-N(14)	100.05(16)				
		O(8)#3-Na(4)-O(9)#3	81.62(14)				
		O(10)-Na(4)-O(9)#3	87.70(16)				
		N(14)-Na(4)-O(9)#3	95.33(15)				
		O(8)#3-Na(4)-N(36)	82.85(14)				
		O(10)-Na(4)-N(36)	164.82(17)				
		N(14)-Na(4)-N(36)	93.24(16)				
		O(9)#3-Na(4)-N(36)	83.76(16)				
		O(8)#3-Na(4)-N(34)#4	92.49(14)				
		O(10)-Na(4)-N(34)#4	94.27(16)				
		N(14)-Na(4)-N(34)#4	90.37(16)				
		O(9)#3-Na(4)-N(34)#4	173.55(15)				

		N(36)-Na(4)-N(34)#4	92.94(16)				
		O(8)#3-Na(4)-Na(3)#3	42.16(10)				
		O(10)-Na(4)-Na(3)#3	94.45(12)				
		N(14)-Na(4)-Na(3)#3	133.89(14)				
		O(9)#3-Na(4)-Na(3)#3	41.56(10)				
		N(36)-Na(4)-Na(3)#3	70.89(12)				
		N(34)#4-Na(4)-Na(3)#3	132.06(11)				
		Na(3)-O(7)-Na(1)	115.91(17)				
		Na(2)-O(1)-Na(1)	102.39(16)				
		Na(1)-O(2)-Na(2)	97.61(16)				
		Na(3)-O(8)-Na(4)#2	95.39(13)				
		Na(3)-O(9)-Na(4)#2	94.63(14)				
		C(13)-N(13)-Na(3)#1	130.9(4)				
		C(15)-N(15)-Na(1)	136.3(4)				
		C(38)-N(38)-Na(1)	170.5(4)				
		N(36)-Na(4)-N(34)#4	92.94(16)				
		O(8)#3-Na(4)-Na(3)#3	42.16(10)				

		O(10)-Na(4)-Na(3)#3	94.45(12)				
		N(14)-Na(4)-Na(3)#3	133.89(14)				
		O(9)#3-Na(4)-Na(3)#3	41.56(10)				
		N(36)-Na(4)-Na(3)#3	70.89(12)				
		N(34)#4-Na(4)-Na(3)#3	132.06(11)				
		Na(3)-O(7)-Na(1)	115.91(17)				
		Na(2)-O(1)-Na(1)	102.39(16)				
		Na(1)-O(2)-Na(2)	97.61(16)				
		Na(3)-O(8)-Na(4)#2	95.39(13)				
		Na(3)-O(9)-Na(4)#2	94.63(14)				
		C(13)-N(13)-Na(3)#1	130.9(4)				
		C(15)-N(15)-Na(1)	136.3(4)				
		C(38)-N(38)-Na(1)	170.5(4)				

Symmetry transformations used to generate equivalent atoms for **1**:

#1 $-x+1, -y, -z+2$ #2 $x-1, y, z$ #3 $x+1, y, z$ #4 $-x+2, -y, -z+1$

Symmetry transformations used to generate equivalent atoms for **2**:

#1 $x-1, y, z$ #2 $-x+1, -y+1, -z+1$ #3 $-x+2, -y+1, -z+1$

#4 $-x+2, -y+2, -z+1$ #5 $x+1, y, z$

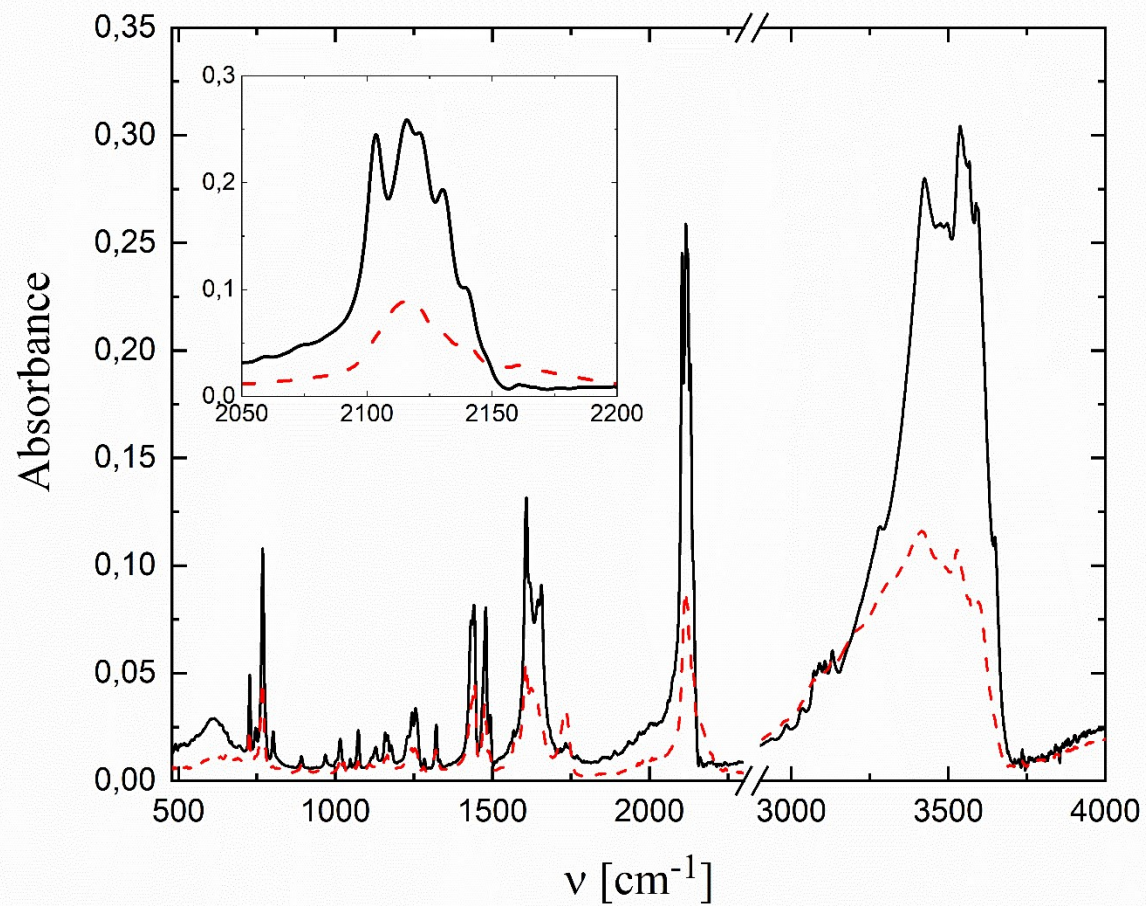


Figure S1. IR spectra for **1** (black, solid line) and **2** (red, dashed line).