Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

15-Copper(II)-Containing 36-Tungsto-4-silicates(IV) $[Cu_{15}O_2(OH)_{10}X(A\text{-}\alpha\text{-}SiW_9O_{34})_4]^{25-}$ (X = Cl, Br): Synthesis, Structure, Magnetic Properties, and Electrocatalytic CO_2 Reduction

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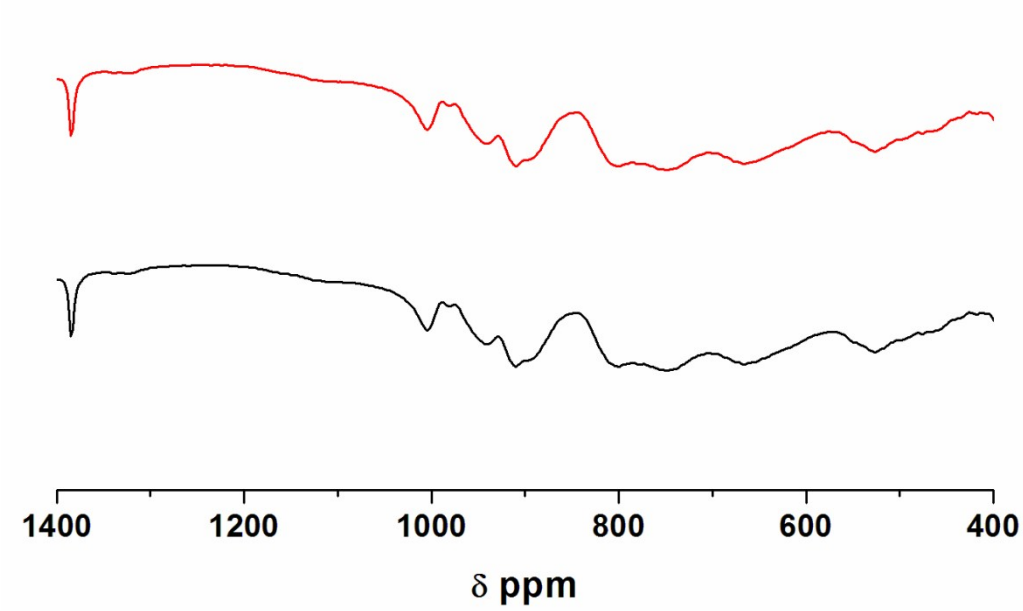

Figure S1. Infrared spectra of **NaK-1** (black) and **NaK-2** (red).

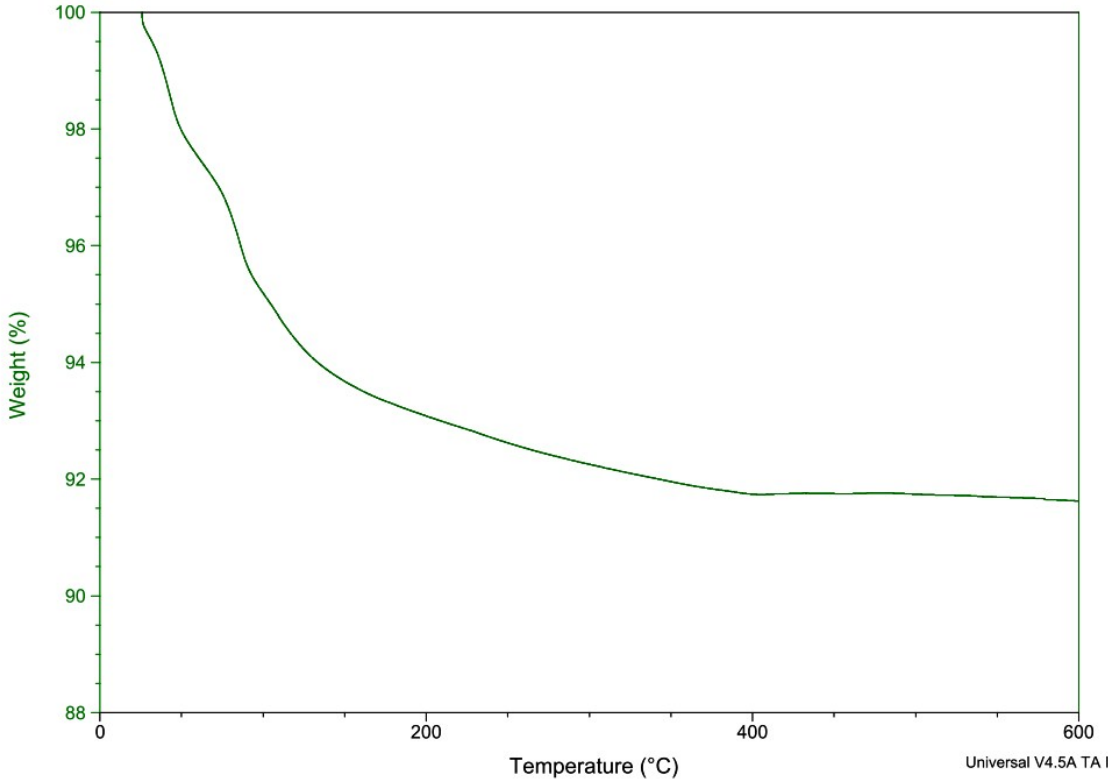

Figure S2. Thermogram of **KNa-1**.

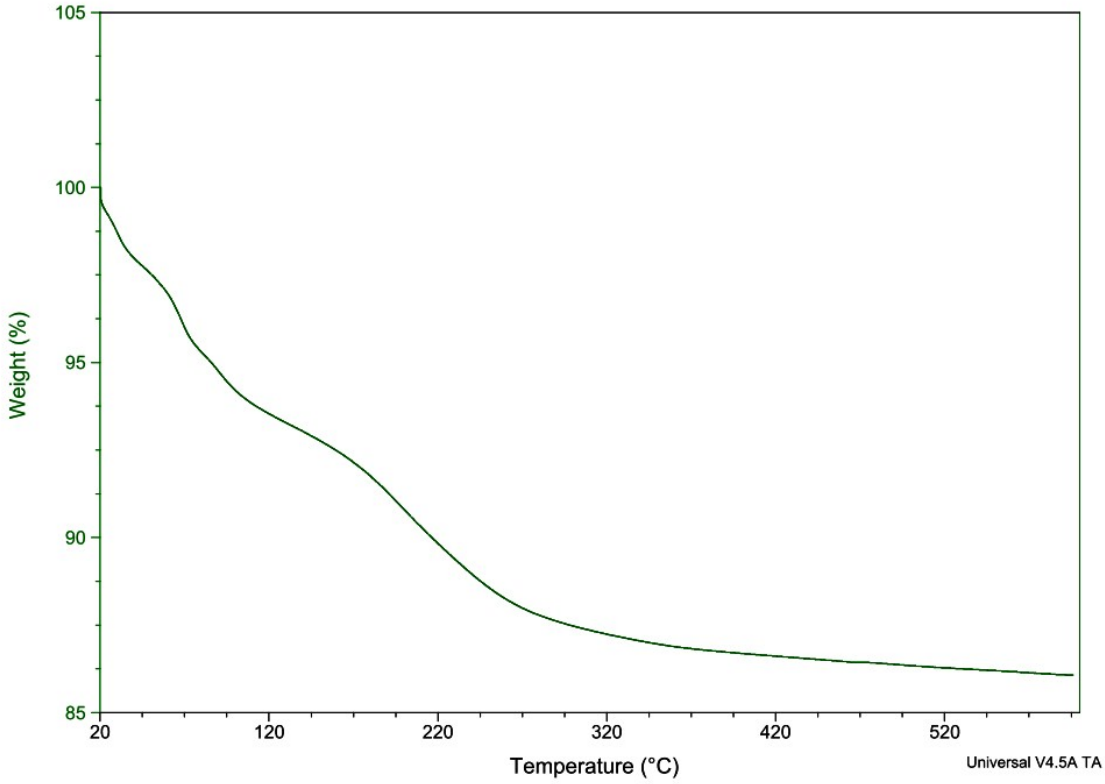

Figure S3. Thermogram of **KNa-2**.

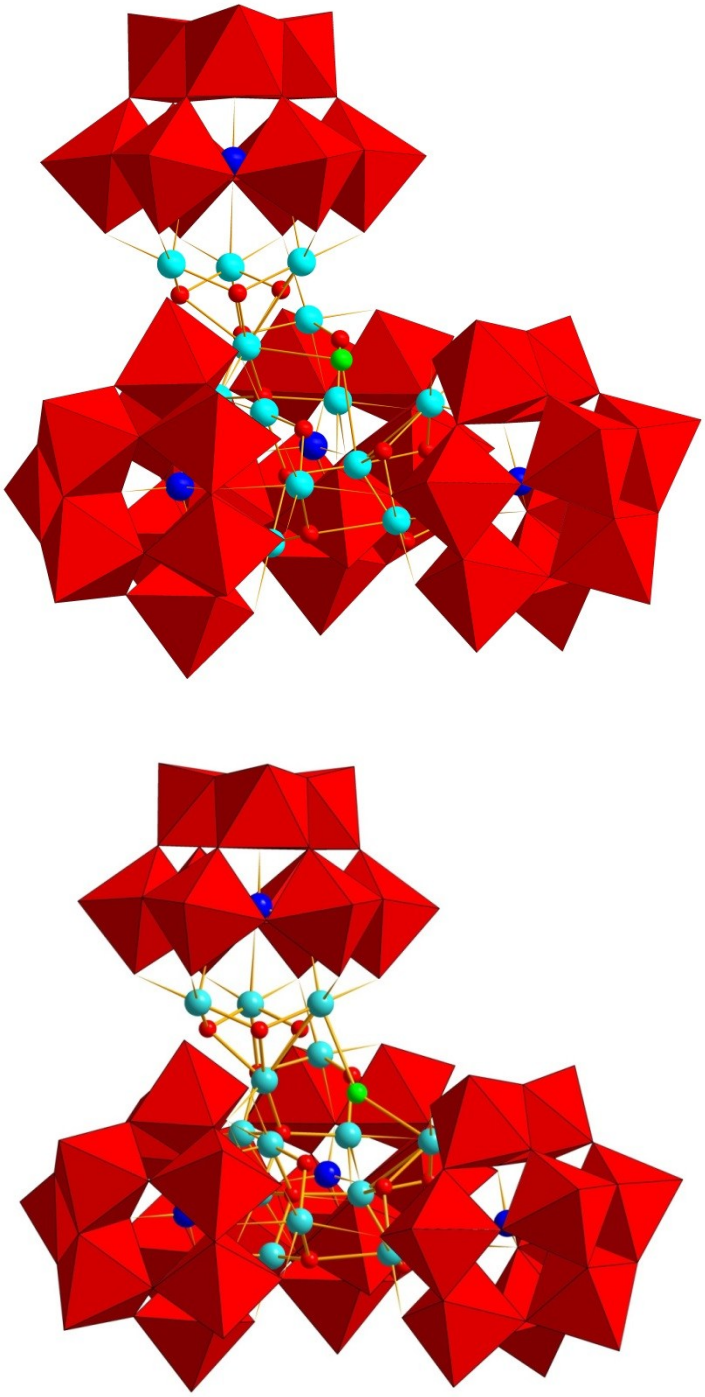

Figure S4. Polyhedral and ball-and-stick representation of Mialane's $[Cu_{14}(OH)_{12}X(A\text{-}\alpha\text{-}SiW_9O_{34})_2(A\text{-}\alpha\text{-}SiW_9O_{33}(OH))_2]^{23-}$ (top) versus our $[Cu_{15}O_2(OH)_{10}X(A\text{-}\alpha\text{-}SiW_9O_{34})_4]^{25-}$ (bottom) Color code: red octahedra (WO_6), blue balls (Si), turquoise balls (Cu), red balls (O), light green ball (Cl).

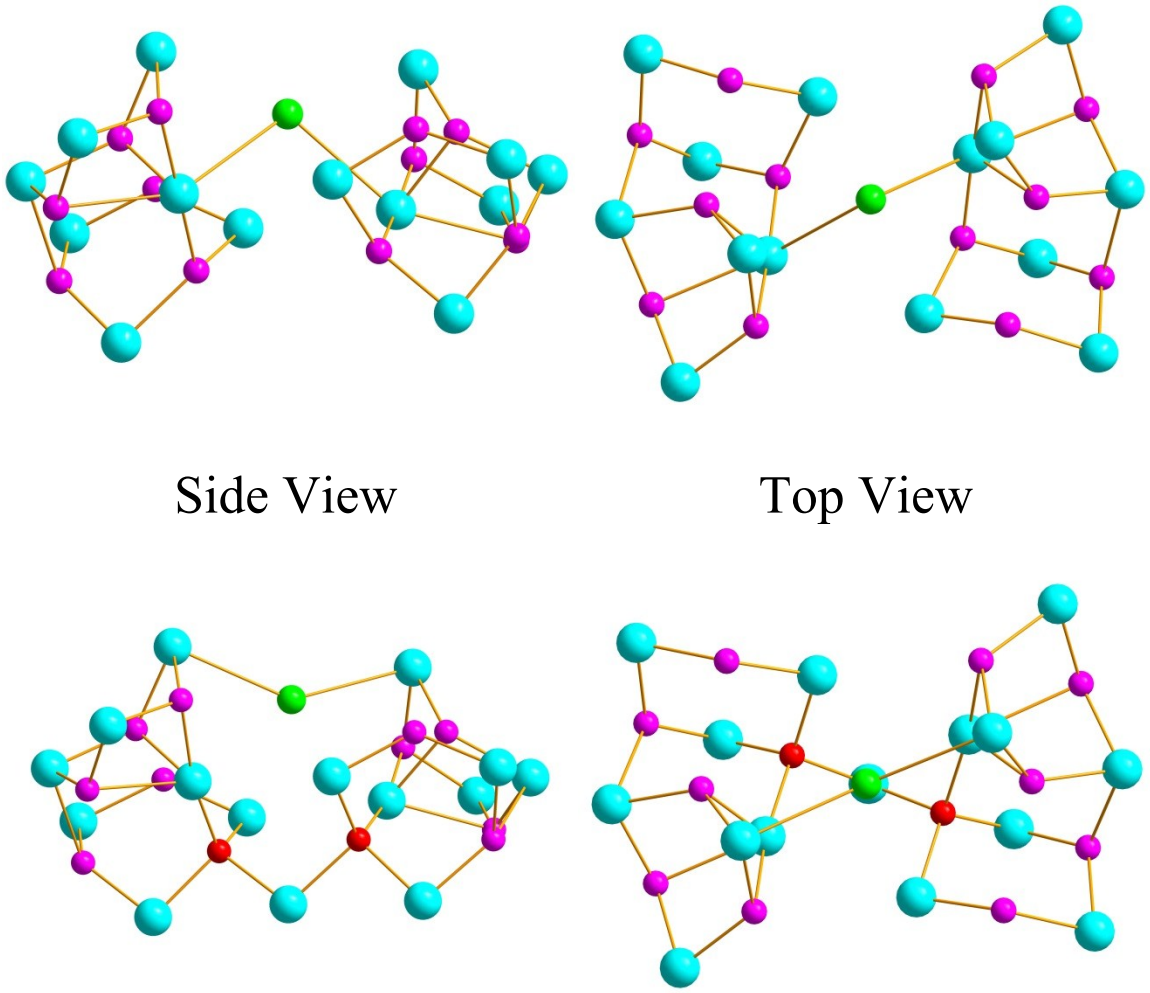

Figure S5. Ball-and-stick representation of Mialane's $\{Cu_{14}(OH)_{12}X\}^{15+}$ (top) versus our $\{Cu_{15}O_2(OH)_{10}X\}^{15+}$ core (bottom). Color code same as in Figure S4.

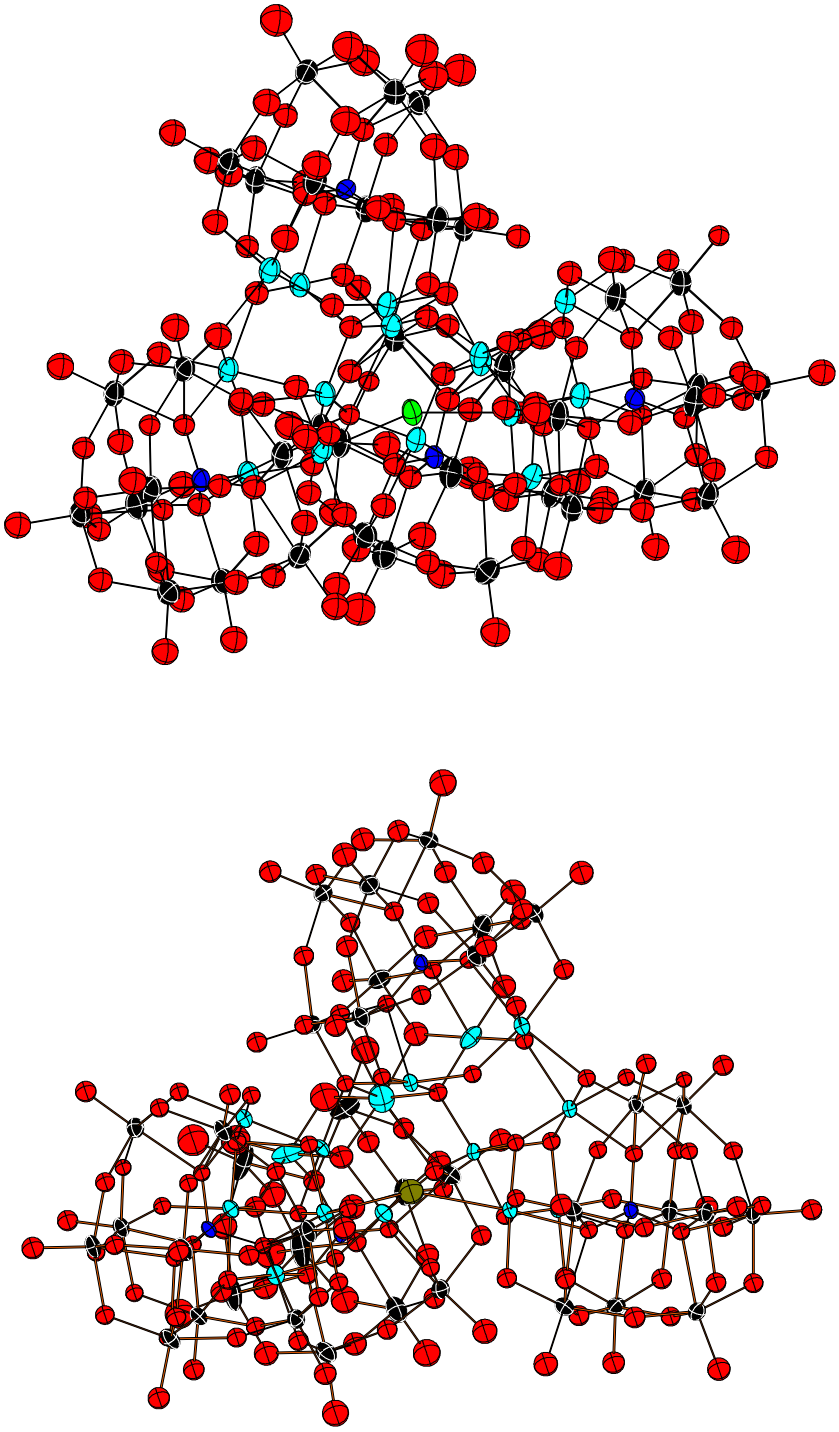

Figure S6. ORTEP representation of polyanions **1** (top) and **2** (bottom).

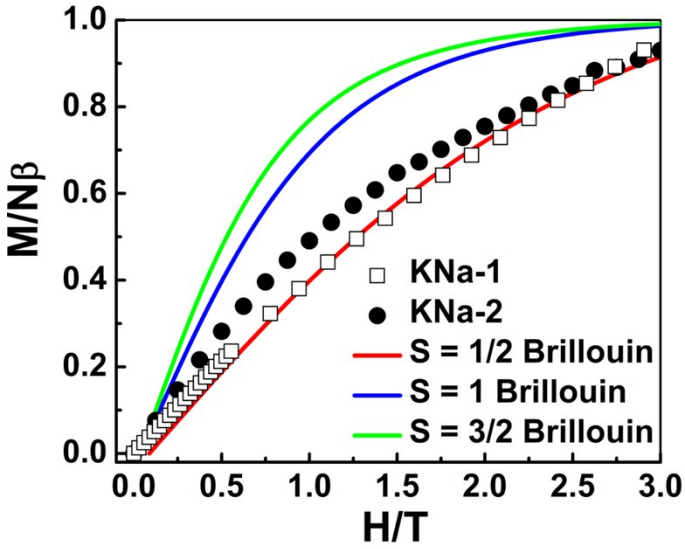

Figure S7. Normalized magnetization of **KNa-1** and **KNa-2** at 1.8 K plotted with the Brillouin function for S = ½, 1, and $^3/_2$. The curvature of both compounds matches closely with the S = ½ function up to 6 T.

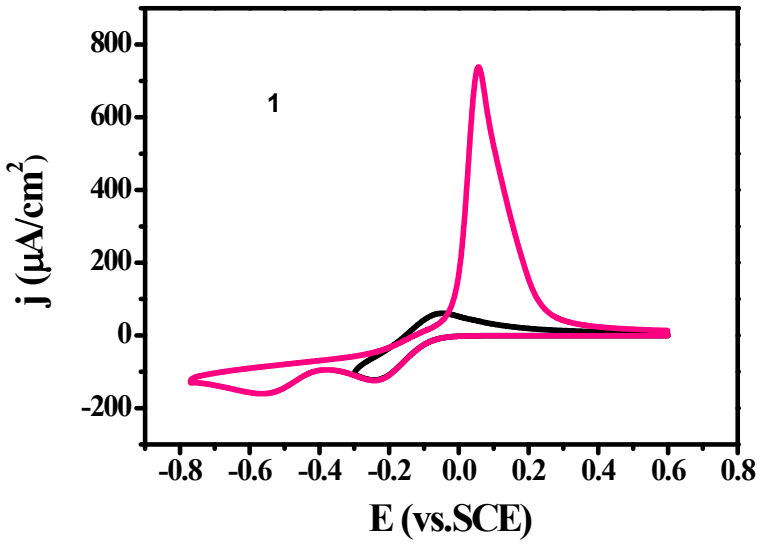

Figure S8. Cyclic voltammograms of 0.1 mM solution of **1** restricted to the Cu^{II}-to-Cu^{I} (black) and Cu^{II}-to-Cu^{0} (red) redox processes, run in 1M CH_3COOLi /CH_3COOH (pH 5), at 100 mV s^{-1}.

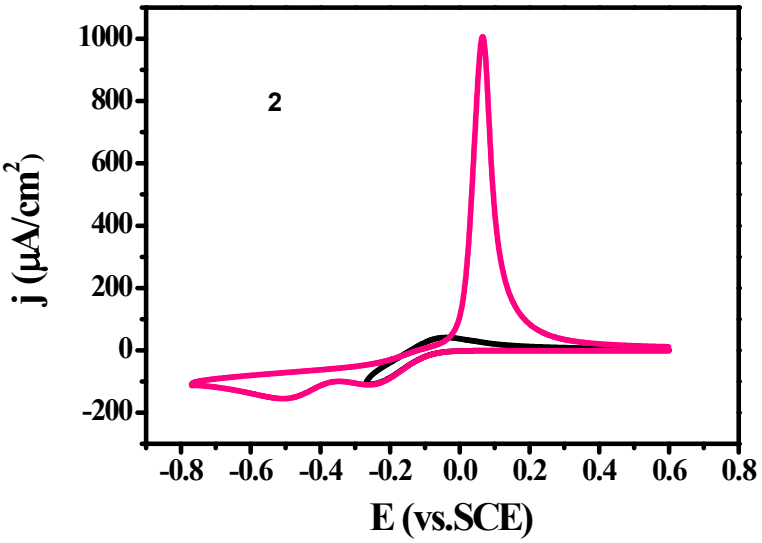

Figure S8. Cyclic voltammograms of 0.1 mM solution of **2** restricted to the Cu^{II}-to-Cu^{I} (black) and Cu^{II}-to-Cu^{0} (red) redox processes, run in 1M CH_3COOLi /CH_3COOH (pH 5), at 100 mV s^{-1}.

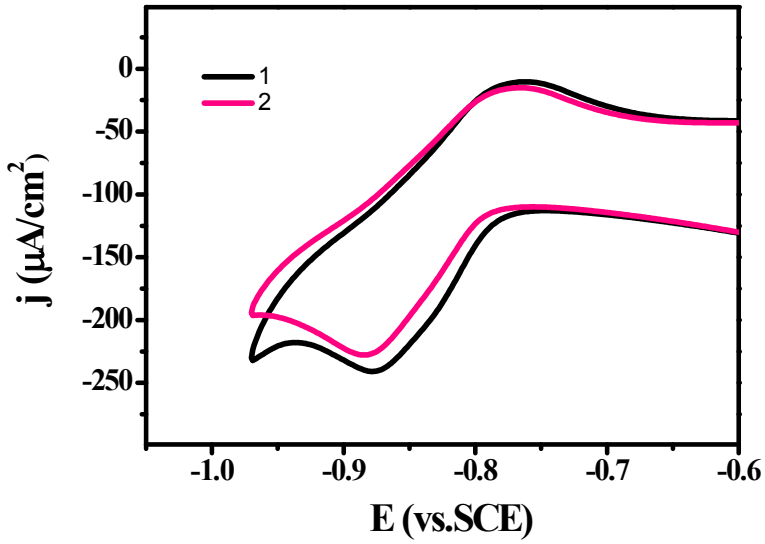

Figure S10. Comparison of the cyclic voltammograms of 0.1 mM solutions of **1** (black) and **2** (red) restricted to the redox processes associated with the W^{VI} centers, run in 1M CH_3COOLi /CH_3COOH (pH 5), at 100 mV s^{-1}.

Table S1. Crystallographic data for **KNa-1** and **KNa-2**.

Compound	**KNa-1**	**KNa-2**
Formula	$Na_{3.5}K_{21.5}[Cu_{15}O_2(OH)_{10}(SiW_9O_{34})_4Cl]$ ·$55H_2O$	$Na_3K_{22}[Cu_{15}O_2(OH)_{10}(SiW_9O_{34})_4Br]$ ·$60H_2O$
Formula weight, g/mol	12009.58	12152.17
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	19.2429(6)	19.2051(12)
b, Å	20.9195(5)	20.8590(12)
c, Å	26.4944(8)	26.3973(16)
α, °	106.8890(10)	106.961(2)
β, °	101.894(2)	102.573(2)
γ, °	90.921(2)	90.741(2)
Volume, $Å^3$	9953.4(5)	9839.0(10)
Z	2	2
D_{calc}, g/cm^3	4.007	4.102
Absorption coefficient	22.884	23.352
F(000)	10726	10870
Crystal size, mm	0.26 x 0.23 x 0.12	0.12 x 0.09 x 0.04
Theta range for data	3.403 - 26.372	3.410 – 26.372
Completeness to Θ_{max},	98.9	99.4
Index ranges	-24 >h>24 , -26>k>26 , -33>l>33	-19<h<24 , -26<k<26 , -32<l<32
Total Reflections	272948	326448
Independent	40215	39975
Calculated Reflections	24967	24085
R(int)	0.1094	0.1294
Data / restraints /	40215 / 0 / 1362	39975 / 0 / 1372
Goodness-of-fit on F2	1.002	1.003
R_1[a]	0.0788	0.0985
wR_2 [b]	0.2662	0.2860
e Density max / min, e.	4.455 / -3.287	4.374 / -3.696

[a] $R_1 = \sum | |F_o| — |F_c| | / \sum |F_o|$. [b] $wR_2 = [\sum w (F_o^2 — F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

Table S2. Selected bond valence sum (BVS) values for **1** (upper) and **2** (lower).

$[Cu_{15}O_2(OH)_{10}(A\text{-}\alpha\text{-}SiW_9O_{34})_4Cl]^{25-}$ (1)

μ_2-O (3Cu-O)	**BVS Value**	**μ_2-O (3Cu-O)**	**BVS Value**
O34C	-0.90	O67C	-0.73
μ_3-O (3Cu-O)	**BVS Value**	**μ_3-O (3Cu-O)**	**BVS Value**
O23C	-1.04	059C	-1.05
O24C	-1.04	O91C	-1.05
O14C	-1.19	O81C	-1.10
O15C	-1.13	O82C	-1.12
μ_4-O (4Cu-O)	**BVS Value**	**μ_4-O (4Cu-O)**	**BVS Value**
O45C	-1.61	O55C	-1.60

$[Cu_{15}O_2(OH)_{10}(A\text{-}\alpha\text{-}SiW_9O_{34})_4Br]^{25-}$ (2)

μ_2-O (3Cu-O)	**BVS Value**	**μ_2-O (3Cu-O)**	**BVS Value**
O34C	-0.91	O67C	-0.75
μ_3-O (3Cu-O)	**BVS Value**	**μ_3-O (3Cu-O)**	**BVS Value**
O93C	-1.08	O26C	-1.13
O81U	-1.09	O14U	-1.32
O91C	-1.09	O24C	-1.05
O81C	-1.09	014C	-1.27
μ_4-O (4Cu-O)	**BVS Value**	**μ_4-O (4Cu-O)**	**BVS Value**
O15C	-1.61	O45C	-1.57