

Article

Study of the Counter Cation Effects on the Supramolecular Structure and Electronic Properties of a Dianionic Oxamate-Based $\{Ni^{II}_2\}$ Helicate

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Chart 1: View of H_4mpba -based compounds since the first publication in 2001. Legend: the flags represent the number of published compounds with transition metal ions whereas the stars indicate the number of published compounds containing only Ni^{II} ions in each year. More details in Table S1.

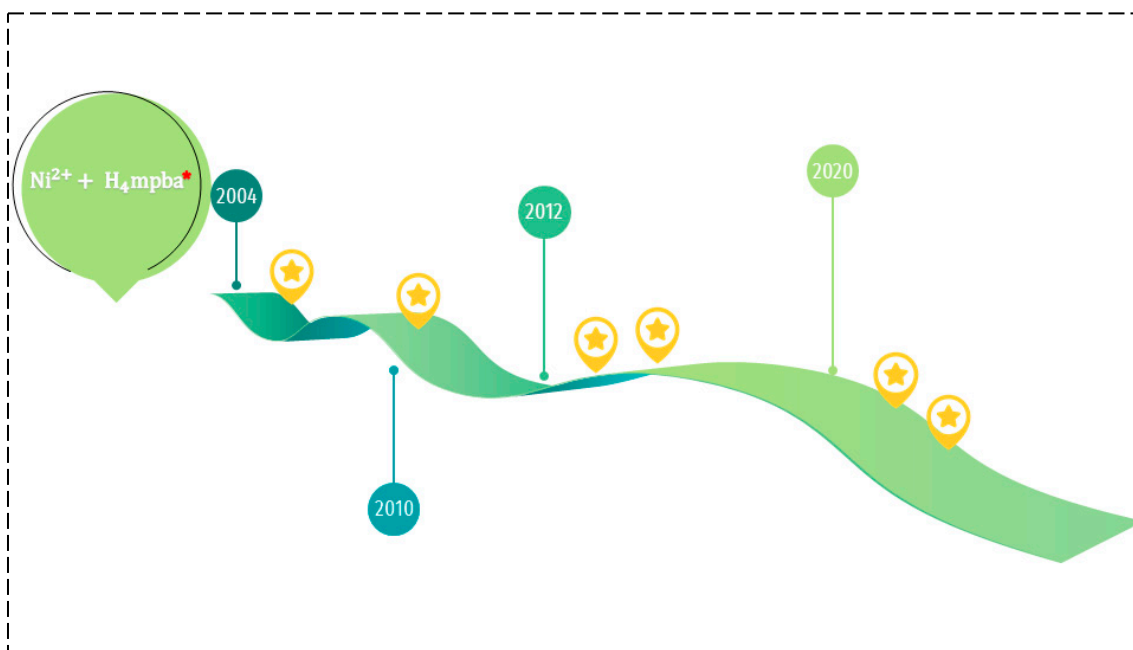
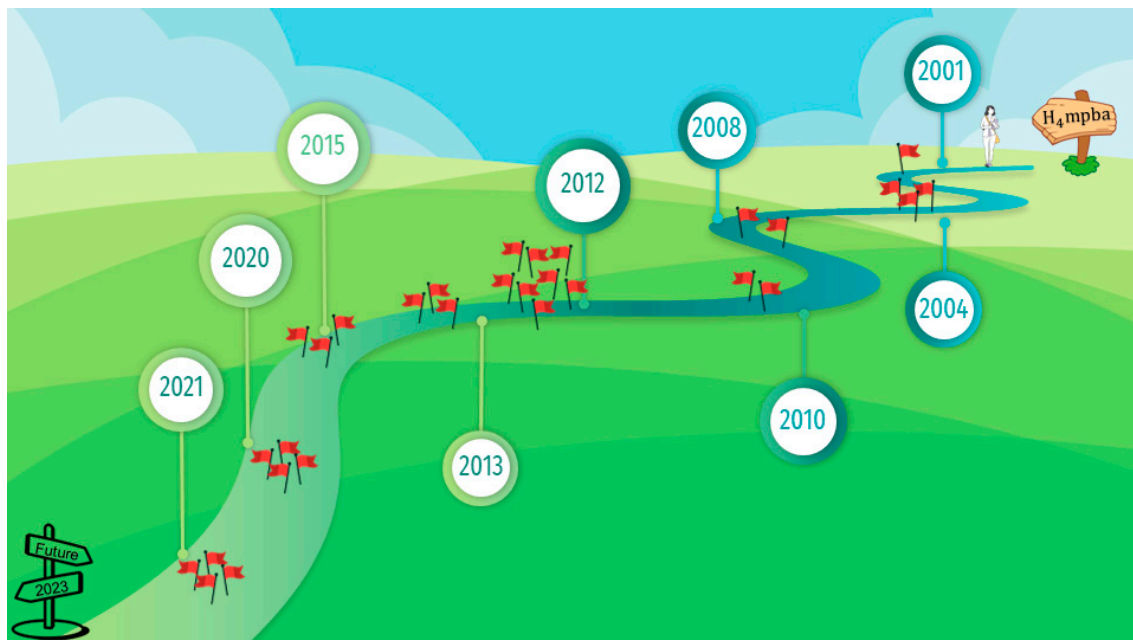
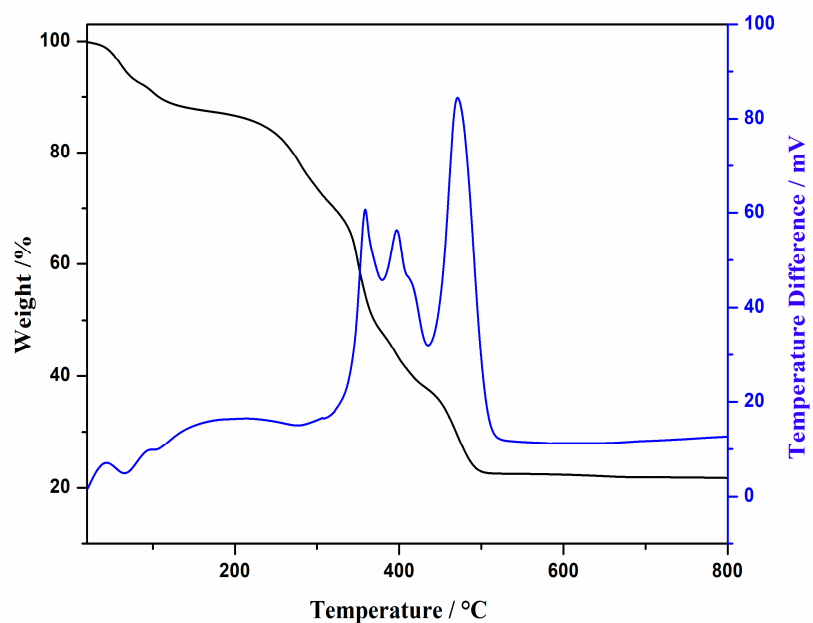
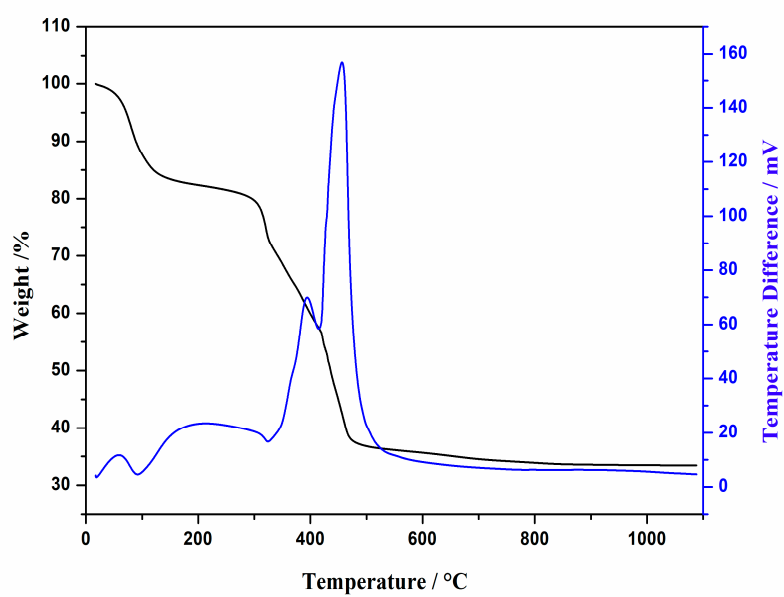


Table S1. Compounds containing the di-deprotonated ($\text{H}_2\text{mpba}^{2-}$) and fully deprotonated (mpba^{4-}) forms of the 1,3-phenylenebis(oxamic) acid (H_4mpba).

Molecular formula	Database identifier	Year	Reference
$\text{Na}_4[\text{Cu}_2(\text{mpba})_2] \cdot 10\text{H}_2\text{O}$	VODXUH	2001	1
$[\text{Co}_2\text{Cu}_2(\text{mpba})_2(\text{H}_2\text{O})_6] \cdot 6\text{H}_2\text{O}$	-	2004	1
$\text{Na}_8[\text{Ni}_2(\text{mpba})_3] \cdot 10\text{H}_2\text{O}$	FAJFIG	2004	2
$\{[\text{Cu}_2(\text{mpba})_2][\text{Cu}(\text{tmen})]_4\}(\text{ClO}_4)_4 \cdot 6\text{H}_2\text{O}$	IYAVUZ	2004	3
$\text{Li}_5[\text{Li}_3\text{Co}_2(\text{mpba})_3(\text{H}_2\text{O})_6] \cdot 31\text{H}_2\text{O}$	POBNEA	2008	4
$\text{Li}_2[\text{Mn}_3\text{Co}_2(\text{mpba})_3(\text{H}_2\text{O})_6] \cdot 22\text{H}_2\text{O}$	-	2008	4
$\text{Na}_2\{[\text{Cu}_2(\text{mpba})_3][\text{Cu}(\text{Me}_5\text{dien})]_6\}(\text{ClO}_4)_6 \cdot 12\text{H}_2\text{O}$	-	2010	5
$\text{Na}_2\{[\text{Ni}_2(\text{mpba})_3][\text{Cu}(\text{Me}_5\text{dien})]_6\}(\text{ClO}_4)_6 \cdot 12\text{H}_2\text{O}$	-	2010	5
$[\text{Na}(\text{H}_2\text{O})_4]_4[\text{Mn}_4\{\text{Cu}_2(\text{mpba})_2(\text{H}_2\text{O})_4\}_3] \cdot 56 \cdot 5\text{H}_2\text{O}$	DAPXID	2012	6
$\text{Na}_8[\text{Ni}^{\text{II}}_2(\text{mpba})_3] \cdot 15\text{H}_2\text{O}$	VEHNED	2012	7
$\text{Na}_8[\text{Co}^{\text{II}}_2(\text{mpba})_3] \cdot 17\text{H}_2\text{O}$	VEHNIH	2012	7
$\text{TBA}_2[\text{Co}_2(\text{H}_2\text{mpba})_3] \cdot 2\text{DMF} \cdot 5\text{H}_2\text{O}$	KEVKON	2012	8
$(\text{HNEt}_3)_2[\text{Co}_2(\text{H}_2\text{mpba})_3] \cdot 6\text{DMF} \cdot 5\text{H}_2\text{O}$	KEVKUT	2012	8
$\text{TBA}_2[\text{Ni}_2(\text{H}_2\text{mpba})_3] \cdot 2\text{DMF} \cdot 2.5\text{H}_2\text{O}$	-	2012	8
$[\text{Mn}_4(\text{H}_2\text{mpba})_4(\text{H}_2\text{O})_{12}]\{[\text{Mn}_8\text{Cu}_8(\text{mpba})_8(\text{H}_2\text{O})_{24}]\} \cdot 29.5\text{H}_2\text{O}$	QEJSEF	2012	9
$[\text{Mn}_4\text{Cu}_4(\text{mpba})_4(\text{H}_2\text{O})_9] \cdot 14\text{H}_2\text{O}$	QEJSIJ	2012	9
$(\text{S})-(1\text{-PhEt})\text{Me}_3\text{N}_2[\text{Mn}_2(\text{ox})\text{Cu}_2(\text{mpba})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$	IDORAW	2013	10
$[\text{Cu}(\text{bipy})(\text{H}_2\text{mpba})]_2 \cdot 2\text{H}_2\text{O}$	-	2013	10
$[\text{Cu}(\text{bipy})(\text{H}_2\text{mpba})] \cdot \text{dmsO}$	-	2013	10
$\text{K}_4[\text{Pd}_2(\text{mpba})_2] \cdot 4\text{H}_2\text{O}$	BUBGIQ	2015	11
$\{[\text{K}_4(\text{H}_2\text{O})(\text{dmsO})][\text{Pd}_2(\text{mpba})_2]\}$	BUBHIR	2015	11
$\{[\text{Cu}(\text{bpca})]_4[\text{Pd}_2(\text{mpba})_2] \cdot 6\text{H}_2\text{O}$	BUBHOX	2015	11
$\{[\text{K}_2(\text{dmf})_2(\text{H}_2\text{O})_2][\text{Co}_2(\text{H}_2\text{mpba})_3] \cdot 2\text{H}_2\text{O}\}_n$	GUDHIZ	2020	12
$\{[\text{K}_2(\text{dmf})_2(\text{H}_2\text{O})_2][\text{Ni}_2(\text{H}_2\text{mpba})_3] \cdot 2\text{H}_2\text{O}\}_n$	GUDHOF	2020	12
$[\text{Co}(\text{tppz})_2][\text{Co}_2(\text{H}_2\text{mpba})_3] \cdot 9\text{H}_2\text{O}$	GUDHUL	2020	12
$[\text{Ni}(\text{tppz})_2][\text{Ni}_2(\text{H}_2\text{mpba})_3] \cdot 9\text{H}_2\text{O}$	GUDJAT	2020	12
$[\text{Co}(\text{H}_2\text{O})_6][\text{Co}_2(\text{H}_2\text{mpba})_3] \cdot 2\text{H}_2\text{O} \cdot 0.5\text{dmsO}$	UYIQEB	2021	13
$[\text{Co}(\text{H}_2\text{O})_6][\text{Co}_2(\text{H}_2\text{mpba})_3] \cdot 3\text{H}_2\text{O} \cdot 0.5\text{dpss}$	UYIQIF	2021	13
$[\text{Co}_2(\text{H}_2\text{mpba})_2(\text{H}_2\text{O})_4]_n \cdot 4n\text{H}_2\text{O}$	UYIQR	2021	13
$[\text{Co}_2(\text{H}_2\text{mpba})_2(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_2]_n \cdot 0.5n\text{H}_2\text{O} \cdot 2ndpss$	UYIQOL	2021	13

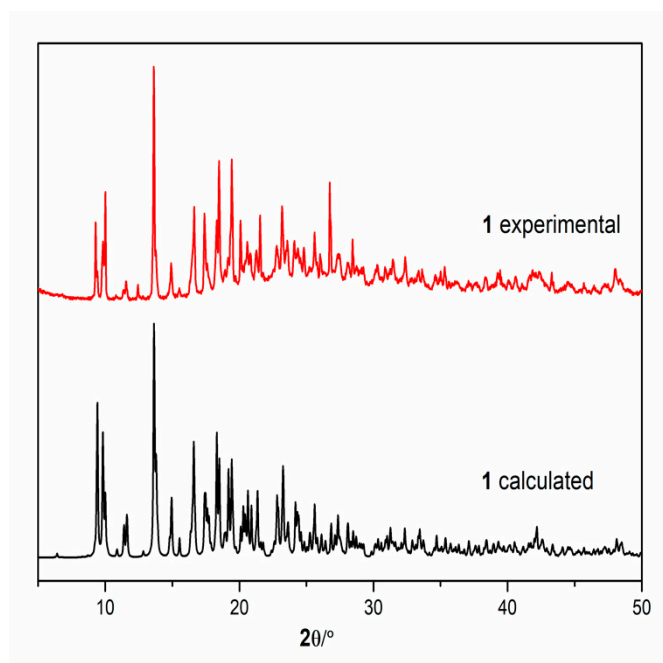


(a)

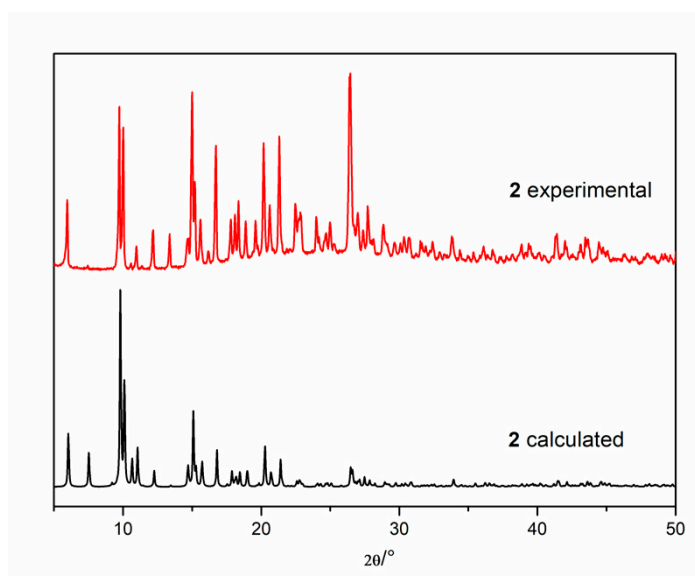


(b)

Figure S1. TG and DTA curves for (a) 1 and (b) 2.



(a)



(b)

Figure S2. Experimental (red) and calculated (black) PXRD patterns of (a) **1** and (b) **2**.

Details for the crystallographic description of 1.

The $\text{H}_2\text{mpba}^{2-}$ ligands are coordinated in three different coordination modes (Figure S3): i) one of them adopts the $\mu_4\text{-}\kappa^2\text{O}^7, \text{O}^8$ (Ni1): κO^9 (**1**): $\kappa^2\text{O}^{10}, \text{O}^{11}$ (Ni2): κO^{11} (K1^{iv}) coordination mode. Only the N1 and N2 amide-nitrogen atoms act as hydrogen bond acceptors in this ligand, being involved in the N4-H4A \cdots O19 $^{\text{i}}$ (coordinated dmsO) and N3-H3A \cdots O27 (free water molecule) type interactions. Otherwise, the hydrogen bond donor atoms concern the coordinated water molecules through O24 $^{\text{v}}$ -H24A \cdots O12 and O25 $^{\text{iv}}$ -H25A $^{\text{iv}}$ \cdots O12 contacts. A very weak C22 $^{\text{v}}$ -H22 $^{\text{v}}$ \cdots O7 type interaction also occurs; ii) Another one exhibits a $\mu_5\text{-}\kappa^2\text{O}^{16}, \text{O}^{17}$ (Ni1): $\kappa^2\text{O}^{17}, \text{O}^{18}$ (K2^{iii}): κO^{18} (**K2**): $\kappa^2\text{O}^{13}, \text{O}^{14}$ (Ni2): κO^{14} (K1^{iv}) coordination mode and it also forms hydrogen bonds [N5-H5 \cdots O26 (free water), N6-

H6A...O20^{viii} (lattice dmsO) and O26-H26A...O15(oxamate) and weaker van der Waals contacts [C22-H22...O7^{vii} (oxamate), C2^{vi}-H2^{vi}...O15 (oxamate) and C33-H33A...O14 (oxamate)]; and iii) the third H₂mpba²⁻ ligand exhibits a $\mu_4-\kappa^2O^4,O^5$ (Ni1): κ^2O^1,O^2 (Ni2): κO^2 (K1^{iv}): κO^3 (K1^{viii}) coordination mode. It is also involved in two hydrogen bonds [N1-H1...O26^{ix} and N2-H2A...O27^{ix} (free water molecule)] and a weaker van der Waals contact [C2-H2...O15^{ix} (oxamate)].

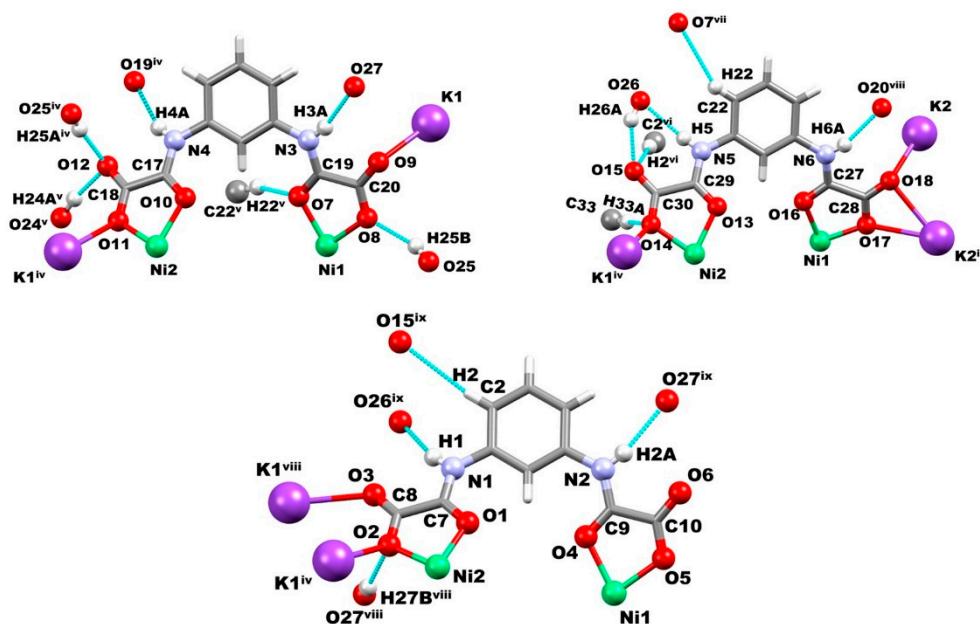


Figure S3. Coordination modes and hydrogen bonds for the H₂mpba²⁻ ligands in the helicate unit. Symmetry code : (iv) = $-x+3/2, y+1/2, -z+1/2$; (v) = $x+1/2, -y+1/2, z+1/2$; (vi) = $x-1, y, z$; (vii) = $x-1/2, -y+1/2, z-1/2$; (viii) = $x+1/2, -y+1/2, z-1/2$; (ix) = $x+1, y, z$; (x) = $-x+2, -y+1, -z$.

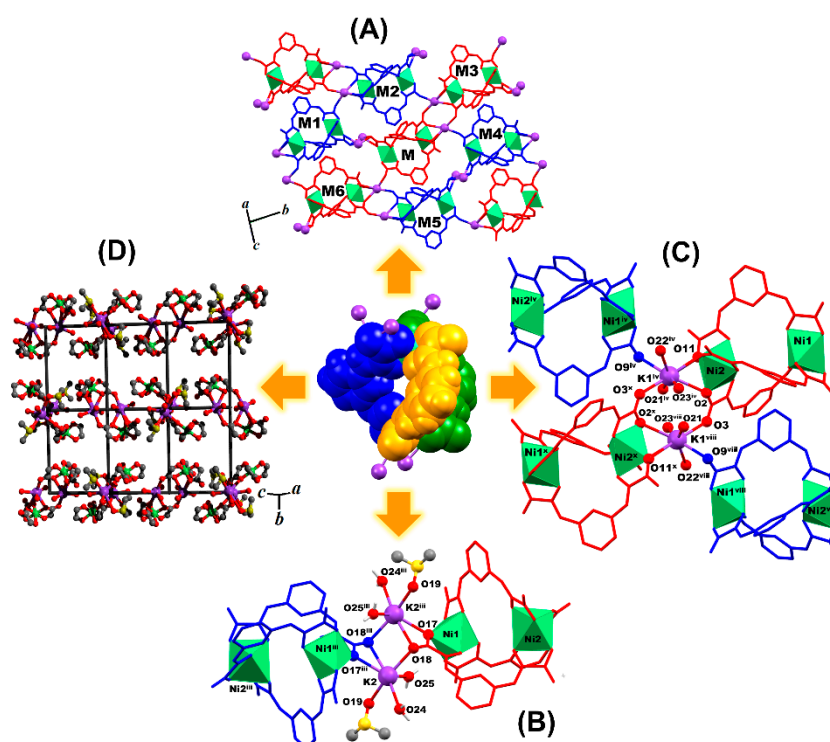


Figure S4. Topological features of the $[\text{Ni}_2(\text{H}_2\text{mpba})_3]^{2-}$ helicate as a molecular building block (MBB) of the $\text{Ni}^{\text{II}}/\text{K}^{\text{I}}$ heterometallic network in **1**. (A) Helicate neighbouring distribution (the **M** helicate as a central unit) in a 2D network along the diagonal of the *ac* plane; the red and blue-capped sticks represent the $[\text{Ni}_2(\text{H}_2\text{mpba})_3]^{2-}$ helicate, the purple spheres concern the K^{I} ions and the green octahedra stand for the Ni^{II} ions. (B) $\text{H}_2\text{O}/\text{dmsO}$ -solvated K^{I} -dinuclear unit, drawn as a central unit and connecting two helicates. (C) Hydrated K^{I} -dinuclear unit, drawn as a central motif and connecting four distinct helicates. (D) Underlying net exhibiting the potassium oxo-metallic disposition in a **sql** topology. Overlap between the 2D underlying net (grid black sticks) with **sql** topology, and the two types of K^{I} -dinuclear units occupying the vertices of the 4,4-connected net [Symmetry code: (i) = $-x + 3/2, y - 1/2, -z + 1/2$; (ii) = $x - 1/2, -y + 1/2, z + 1/2$; (iii) = $-x + 2, -y, -z$; (iv) = $-x + 3/2, y + 1/2, -z + 1/2$; (v) = $x + 1/2, -y + 1/2, z + 1/2$; (vi) = $x - 1, y, z$; (vii) = $x - 1/2, -y + 1/2, z - 1/2$; (viii) = $x + 1/2, -y + 1/2, z - 1/2$; (ix) = $x + 1, y, z$; (x) = $-x + 2, -y + 1, -z$].

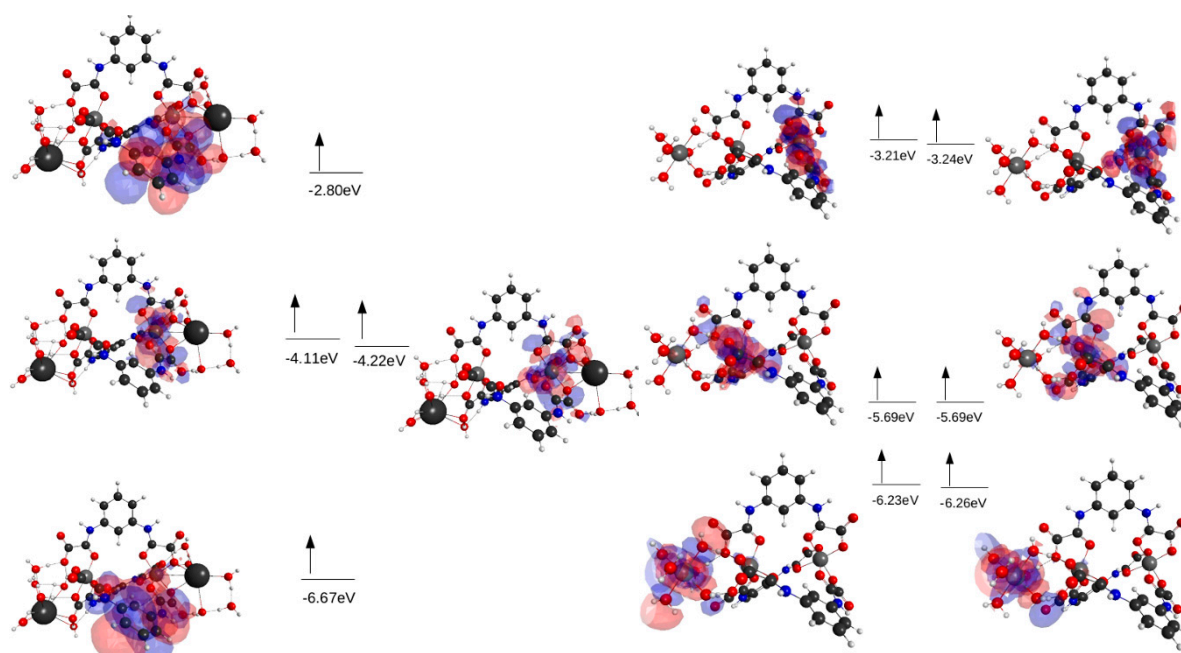


Figure S5. Frontier molecular orbitals calculated at the $\omega\text{B97X-D}/\text{SBKJC}$ level for **1** (left) and **2** (right).

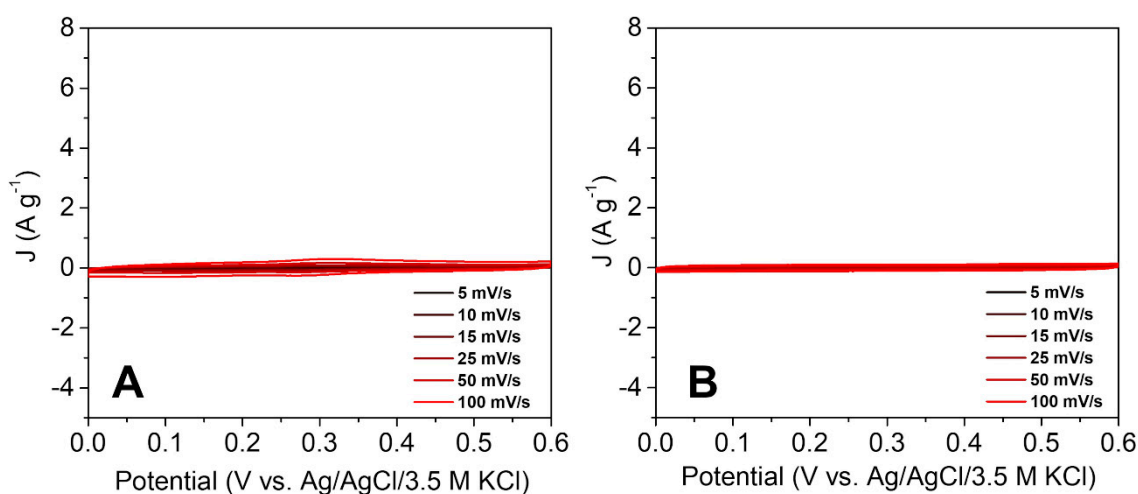


Figure S6. Cyclic voltammograms obtained at different scan rates (5 – 100 mV s^{-1}) for (A) **1** and (B) **2**. Electrolyte: 1.0 M KCl.

Table S2. Selected bond distances, bond angles, hydrogen bonds, and C-H...O type contacts in **1**^{*}.

Geometric parameters for 1					
Bond distances (Å)					
O4-Ni1	2.059 (3)	O1-Ni2	2.054 (3)	O18-K2	2.738 (3)
O5-Ni1	2.033 (3)	O2-Ni2	2.035 (3)	O19-K2	2.682 (4)
O7-Ni1	2.064 (3)	O10-Ni2	2.064 (2)	O24-K2	2.856 (8)
O8-Ni1	2.025 (3)	O11-Ni2	2.022 (3)	O25-K2	2.662 (4)
O16-Ni1	2.059 (3)	O13-Ni2	2.062 (3)	O17 ⁱⁱⁱ -K2	2.849 (3)
O17-Ni1	2.028 (3)	O14-Ni2	2.035 (3)	O18 ⁱⁱⁱ -K2	2.904 (4)
O9-K1	2.760 (3)	O23-K1	3.042 (8)	O11 ⁱ -K1	3.290 (3)
O21-K1	2.756 (6)	O2 ⁱ -K1	2.918 (3)	O14 ⁱ -K1	2.789 (3)
O22-K1	2.962 (5)	O3 ⁱⁱ -K1	2.780 (3)	O18-K2	2.738 (3)
O19-K2	2.682 (4)	O24-K2	2.856 (8)	O25-K2	2.662 (4)
Bond angles (°)					
O8-Ni1-O17	93.23 (11)	O5-Ni1-O16	175.81 (12)	O8-Ni1-O7	81.26 (10)
O8-Ni1-O5	91.99 (12)	O8-Ni1-O4	171.99 (12)	O17-Ni1-O7	170.66 (13)
O17-Ni1-O5	95.82 (12)	O17-Ni1-O4	91.47 (12)	O5-Ni1-O7	91.93 (12)
O8-Ni1-O16	90.57 (12)	O5-Ni1-O4	81.08 (11)	O16-Ni1-O7	91.75 (11)
O17-Ni1-O16	80.72 (12)	O16-Ni1-O4	96.58 (11)	O4-Ni1-O7	94.89 (10)
O11-Ni2-O14	90.88 (12)	O2-Ni2-O1	81.02 (10)	O11-Ni2-O10	81.14 (11)
O11-Ni2-O2	94.10 (11)	O11-Ni2-O13	169.26 (12)	O14-Ni2-O10	90.07 (11)
O14-Ni2-O2	92.96 (11)	O14-Ni2-O13	80.97 (11)	O2-Ni2-O10	174.40 (11)
O11-Ni2-O1	91.93 (12)	O2-Ni2-O13	93.31 (11)	O1-Ni2-O10	96.12 (10)
O14-Ni2-O1	173.53 (11)	O1-Ni2-O13	96.91 (11)	O13-Ni2-O10	91.82 (10)
O21-K1-O9	69.19 (14)	O21-K1-O3 ⁱⁱ	100.85 (15)	O9-K1-O2 ⁱ	139.97 (10)
O21-K1-O22	152.20 (17)	O9-K1-O3 ⁱⁱ	81.05 (9)	O3 ⁱⁱ -K1-O2 ⁱ	127.07 (9)
O9-K1-O22	83.01 (13)	O21-K1-O14 ⁱ	120.26 (14)	O14 ⁱ -K1-O2 ⁱ	62.24 (8)
O21-K1-O23	144.37 (18)	O9-K1-O14 ⁱ	118.48 (9)	O3 ⁱⁱ -K1-O22	74.18 (12)

O9-K1-O23	133.30 (16)	O3 ⁱⁱ -K1-O14 ⁱ	138.24 (11)	O14 ⁱ -K1-O22	72.46 (11)
O22-K1-O23	58.75 (16)	O21-K1-O2 ⁱ	77.01 (13)	O2 ⁱ -K1-O22	128.23 (12)
O3 ⁱⁱ -K1-O23	64.42 (14)	O14 ⁱ -K1-O23	77.01 (13)	O2 ⁱ -K1-O23	86.73 (15)
O21-K1-O11 ⁱ	65.53 (14)	O9-K1-O11 ⁱ	89.22 (9)	O3 ⁱⁱ -K1-O11 ⁱ	165.57 (10)
O14 ⁱ -K1-O11 ⁱ	56.05 (8)	O2 ⁱ -K1-O11 ⁱ	56.77 (7)	O22-K1-O11 ⁱ	115.36 (11)
O25-K2-O19	80.68 (12)	O18-K2-O24	103.52 (17)	O19-K2-O18 ⁱ	98.96 (10)
O25-K2-O18	83.33 (11)	O25-K2-O17 ⁱ	130.90 (16)	O18-K2-O18 ⁱ	80.91 (10)
O19-K2-O18	164.00 (11)	O19-K2-O17 ⁱ	92.87 (10)	O17 ⁱ -K2-O18 ⁱ	45.34 (9)
O25-K2-O24	106.0 (2)	O18-K2-O17 ⁱ	98.12 (10)	O24-K2-O18 ⁱ	166.23 (18)
O19-K2-O24	80.40 (16)	O25-K2-O18 ⁱ	87.35 (16)		

Hydrogen bonds and C-H...O type contacts

D-H...A	<i>d</i> (D...A)/Å	<i>d</i> (H...A)/Å	<(D-H...A)/°
N4-H4A...O19 ⁱ	2.908 (5)	2.090	158.7
N3-H3A...O27	3.032 (5)	2.908 (5)	164.6
O25 ^{iv} -H25A ^{iv} ...O12	2.927 (6)	2.08 (5)	171 (5)
O24 ^v -H24A ^v ...O12	2.952 (8)	1.966	170.9
O25-H25B...O8	2.852 (6)	2.06 (5)	152 (5)
C22 ^v -H22 ^v ...O7	3.831 (5)	2.984	152.1
N5-H5...O26	3.085 (6)	2.229	173.1
N6-H6A...O20 ^{viii}	2.934 (6)	2.103	162.4
C22-H22...O7 ^{vii}	3.831 (5)	2.984	152.1
O26-H26A...O15	2.799 (6)	2.01 (6)	151 (5)
C2 ^{vi} -H2 ^{vi} ...O15	3.723 (6)	2.800	171.7
C33-H33A...O14	3.808 (9)	2.890	160.4
N2-H2A...O27 ^{ix}	3.057 (5)	2.223	163.5
N1-H1...O26 ^{ix}	2.958 (6)	2.128	161.8
C2-H2...O15 ^{ix}	3.723 (6)	2.800	171.7

O26^{ix}–H26A^{ix}...O15^{ix} 2.799 (6) 2.01 (6) 151 (5)

O27^{viii}–H27B^{viii}...O2 3.122 (4) 2.35 (4) 156 (5)

* Symmetry code: (i) = $-x + 3/2, y - 1/2, -z + 1/2$; (ii) = $x - 1/2, -y + 1/2, z + 1/2$; (iii) = $-x + 2, -y, -z$; (iv) = $-x + 3/2, y + 1/2, -z + 1/2$; (v) = $x + 1/2, -y + 1/2, z + 1/2$; (vi) = $x - 1, y, z$; (vii) = $x - 1/2, -y + 1/2, z - 1/2$; (viii) = $x + 1/2, -y + 1/2, z - 1/2$; (ix) = $x + 1, y, z$; (x) = $-x + 2, -y + 1, -z$.

Table S3. Selected bond lengths, bond angles, and hydrogen bonds in **2** *.

Geometric parameters for 2					
Bond distances (Å)					
Ni1–O1	2.033 (2)	Ni1–O7	2.047 (3)	Ni1–O5	2.051 (2)
Ni1–O2	2.078 (2)	Ni1–O8	2.054 (2)	Ni1–O4	2.045 (2)
Ni2–O12	2.026 (3)	Ni2–O10	2.070 (3)	Ni2–O11 ⁱⁱ	2.053 (3)
Ni2–O11	2.053 (3)	Ni2–O12 ⁱⁱ	2.026 (3)	Ni2–O10 ⁱⁱ	2.070(3)
Bond angles (°)					
O1–Ni1–O2	80.30 (9)	O8–Ni1–O2	92.81 (9)	O4–Ni1–O5	80.70 (9)
O1–Ni1–O8	170.70 (10)	O5–Ni1–O2	171.76 (10)	O4–Ni1–O7	170.98 (10)
O1–Ni1–O5	93.06 (9)	O5–Ni1–O8	94.31 (10)	O7–Ni1–O2	94.45 (10)
O1–Ni1–O4	90.04 (10)	O4–Ni1–O2	94.36 (9)	O7–Ni1–O8	80.86 (10)
O1–Ni1–O7	93.37 (11)	O4–Ni1–O8	96.76 (9)	O7–Ni1–O5	90.77 (10)
O12–Ni2–O11	92.68 (13)	O12 ⁱ –Ni2–O11 ⁱ	92.68 (13)	O11–Ni2–O10 ⁱ	89.45 (14)
O11–Ni2–O10	90.55 (14)	O12 ⁱ –Ni2–O10 ⁱ	92.14 (14)	O11 ⁱ –Ni2–O10	89.44 (14)
O12 ⁱ –Ni2–O12	180.0	O12 ⁱ –Ni2–O10	87.86 (14)	O11 ⁱ –Ni2–O10 ⁱ	90.55 (14)
O12 ⁱ –Ni2–O11	87.32 (13)	O12–Ni2–O10 ⁱ	87.86 (14)	O10 ⁱ –Ni2–O10	180.0
O12–Ni2–O11 ⁱ	87.32 (13)	O11–Ni2–O11 ⁱⁱ	180.0	O12–Ni2–O10 ⁱ	87.86 (14)
Hydrogen bonds					
D–H...A	$d(\text{D}\cdots\text{A})/\text{\AA}$	$d(\text{H}\cdots\text{A})/\text{\AA}$	$\angle(\text{D–H}\cdots\text{A})/^\circ$		
N1–H1...O3 ⁱⁱⁱ	2.075	2.882 (4)	155.9		
N2–H2...O6 ^{iv}	2.144	2.972 (4)	161.3		
O12–H12B...O1	1.878	2.684 (4)	157.5		
O10–H10B...O5	1.898	2.718 (4)	161.7		

O11-H11B...O7 2.009 2.801 (4) 154.3

* Symmetry code: (i) = $-x, -y, -z$; (ii) = $-x + 5/4, -y + 1/4, z$; (iii) = $-x + 7/4, y, -z + 7/4$; (iv) = $x, -y + 1/4, -z + 9/4$.

Table S4. Possible geometries of eight-coordinated metal centers and deviation parameters from each ideal polyhedron for Ni and K in 1.

Geometry	Point group	Shape	K1
OP-8	D8h	Octagon	24.559
HPY-8	C7v	Heptagonal pyramid	20.885
HBPY-8	D6h	Hexagonal bipyramid	21.459
CU-8	Oh	Cube	21.227
SAPR-8	D4d	Square antiprism	11.739
TDD-8	D2d	Triangular dodecahedron	11.249
JGBF-8	D2d	Johnson gyrobifastigium J26	15.723
JETBPY-8	D3h	Johnson elongated triangular bipyramid J14	15.973
JBTPR-8	C2v	Biaugmented trigonal prism J50	8.731
BTPR-8	C2v	Biaugmented trigonal prism	11.084
JSD-8	D2d	Snub disphenoid J84	6.921
TT-8	Td	Triakis tetrahedron	21.700
ETBPY-8	D3h	Elongated trigonal bipyramid	20.234

Table S5. Possible geometries of eight-coordinated metal centers and deviation parameters from each ideal polyhedron for Ni in 2.

Geometry	Point group	Shape	K2	Ni1	Ni2
HP-6	D6h	Hexagon	28.392	12.880	13.126
PPY-6	C5v	Pentagonal pyramid	22.555	23.457	23.717
OC-6	Oh	Octahedron	18.969	11.072	11.220
TPR-6	D3h	Trigonal prism	21.598	17.800	18.905
JPPY-6	C5v	Johnson pentagonal pyramid J2	22.324	24.119	23.739

Geometry	Point group	Shape	Ni1	Ni2
HP-6	D6h	Hexagon	24.245	24.047
PPY-6	C5v	Pentagonal pyramid	23.308	27.531
OC-6	Oh	Octahedron	7.411	7.746
TPR-6	D3h	Trigonal prism	15.237	18.086
JPPY-6	C5v	Johnson pentagonal pyramid J2	24.661	29.041

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