

Synthesis, Structural Characterization and Magnetic Behavior of a Ni^{II} 2D Bi-Layer MOF, {[Ni₂(C₅O₅)₂(bpe)₂]·H₂O}_n (bpe = 1,2-bis(4-pyridyl)ethylene)

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Supplementary Materials :

Table S1 C–O and C–C bond lengths (Å) of C₅O₅²⁻ for **1**.

Table S2 π – π interactions (face-to-face) in **1**.

Figure S1 Distorted octahedral coordination sphere about (a) Ni(1) and (b) Ni(2) with atom labeling scheme (ORTEP drawing, 30 % thermal ellipsoids).

Figure S2 Crystal packing of **1** along the *b*-axis showing the formation of a 3D supramolecular architecture by intermolecular π – π interactions.

Figure S3 Thermogravimetric measurement of **1**.

Figure S4 Temperature dependence of magnetic susceptibilities of de-solvated **1** from 300 to 1.8 K in the form of $\chi_M T$ (□) and magnetic moment (B. M.) (○) vs *T*.

Table S1. C–O and C–C bond lengths (Å) of $C_5O_5^{2-}$ for **1**

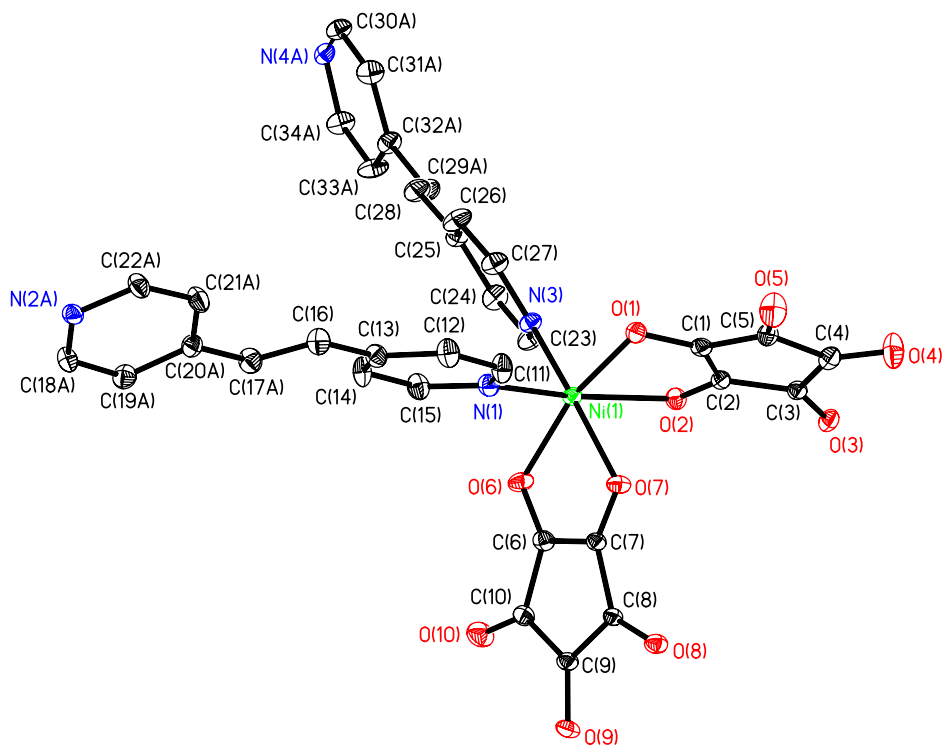
$\mu_3-C_5O_5^{2-}$			
O(1)–C(1)	1.270(4)	C(1)–C(2)	1.416(5)
O(2)–C(2)	1.280(4)	C(2)–C(3)	1.424(5)
O(3)–C(3)	1.260(4)	C(3)–C(4)	1.480(5)
O(4)–C(4)	1.211(5)	C(4)–C(5)	1.500(6)
O(5)–C(5)	1.215(5)	C(5)–C(1)	1.473(5)
$\mu_4-C_5O_5^{2-}$			
O(6)–C(6)	1.248(4)	C(6)–C(7)	1.452(5)
O(7)–C(7)	1.257(4)	C(7)–C(8)	1.451(5)
O(8)–C(8)	1.253(4)	C(8)–C(9)	1.444(5)
O(9)–C(9)	1.250(4)	C(9)–C(10)	1.488(5)
O(10)–C(10)	1.223(5)	C(10)–C(6)	1.481(5)

The croconate ligand acts as a bridging ligand, adopting two different bridging *bis*-bidentate modes. The first one is a bridging *bis*-bidentate mode through three-adjacent (μ_3) croconate oxygen atoms to link Ni ions with the Ni---Ni separation of 4.47 Å. The bond analysis of the C–C and C–O bond lengths of croconate (Table S1) reveals that two uncoordinated oxygens (O(4) and O(5)) show a ketonic form with shorter bond lengths (1.211(5) and 1.215(5) Å for C(4)–O(4) and C(5)–O(5), respectively) compared to the C–O bond lengths (1.270(4), 1.280(4) and 1.260(3) Å for C(1)–O(1), C(2)–O(2) and C(3)–O(3), respectively) of the metal-coordinated oxygen atoms. Notably, the C–C bond lengths, 1.500(6) Å for C(4)–C(5), between two non-bonded C=O groups are close to being single bond in character, and they are also longer than other C–C bond lengths (1.416(5) – 1.480(5) Å), indicating a partial π -electron localization form of croconate in the five-membered ring. Such partial π -electron localization molecular geometry of $C_5O_5^{2-}$ seems to be in accordance with charge-localized form of croconate in a hydrogen-bonded host lattice, alkali metal croconate salts and theoretical predictions. The other one also adopts a bridging *bis*-bidentate mode, but through four-adjacent croconate oxygen atoms (μ_4), to link Ni ions with the Ni---Ni separation of 6.954(6) Å. The uncoordinated oxygen atom (O(10)) also shows a ketonic form with shorter bond lengths (1.223(5) Å for C(10)–O(10)) compared to other C–O bond lengths (1.248(5)–1.257(4) Å) of the metal-coordinated oxygen atoms. The differences among five C–C bond lengths ((STable 1)) of μ_4 -croconate are not so obvious and in the range of 1.444(5)–1.488(5) Å, indicating an intermediate pattern between the charge-localized (C_{2v}) and charge-delocalized (D_{5h}) forms of croconate upon complexation.

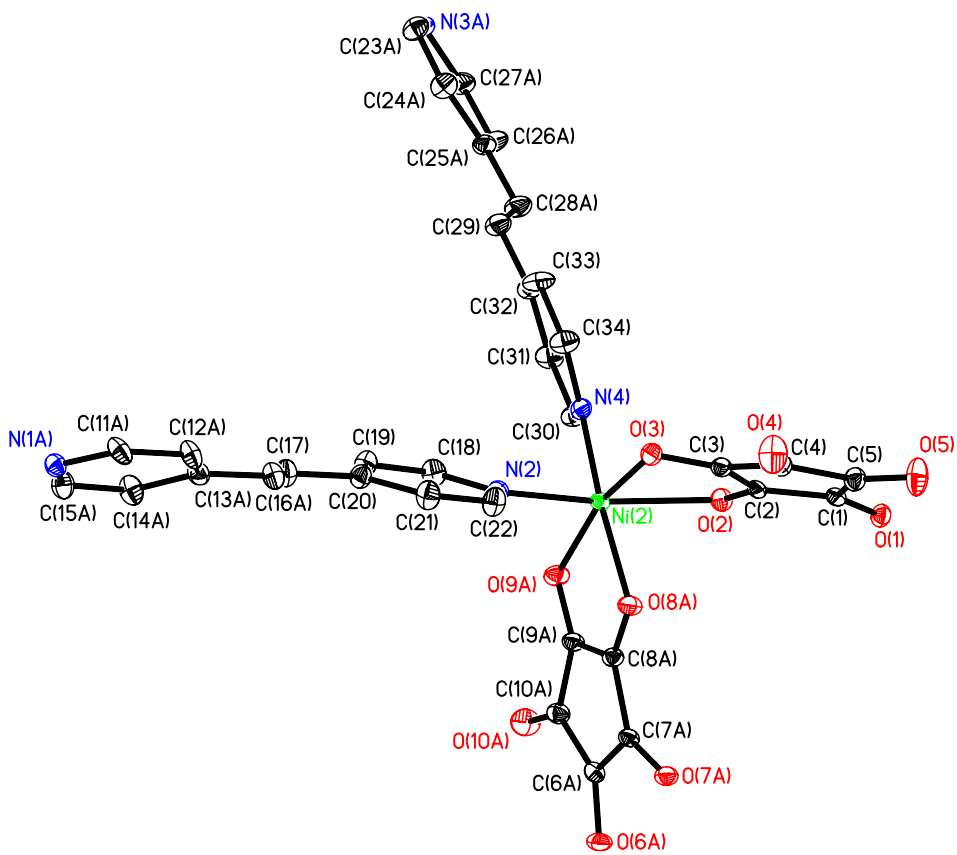
Table S2 π - π interactions (face-to-face) in **1**^a

Ring(i) → Ring(j)	Dihedral Angle (i,j)/°	Slip angle (i,j)/°	Distance of centroid(i) form ring(j)/Å	Distance between the (i,j) ring centroids/Å
R(1) → R(2) _i	11.3	30.1	3.589	4.152
R(2) → R(1) _i	11.3	40.6	3.154	4.152
R(1) → R(3) _{ii}	21.8	21.6	3.894	4.188
R(3) → R(1) _{ii}	21.8	38.8	3.262	4.188

^a Symmetry code: (i) = $-x+1, y+3/2, -z+3/2$; (ii) = $-x+1, y+3/2, -z+5/2$. R(i)/R(j) denotes the centroids of i-th/j-th of bpe/croconate; R(1) = C(1)–C(2)–C(3)–C(4)–C(5); R(2) = N(1)–C(11)–C(12)–C(13)–C(14)–C(15); R(3) = N(2)–C(18)–C(19)–C(20)–C(21)–C(22).



(a)



(b)

Figure S1

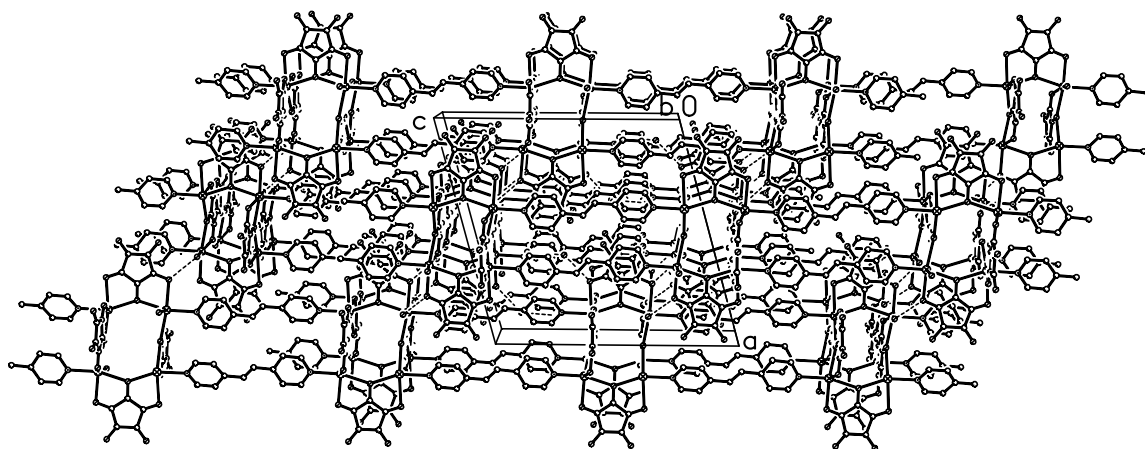


Figure S2

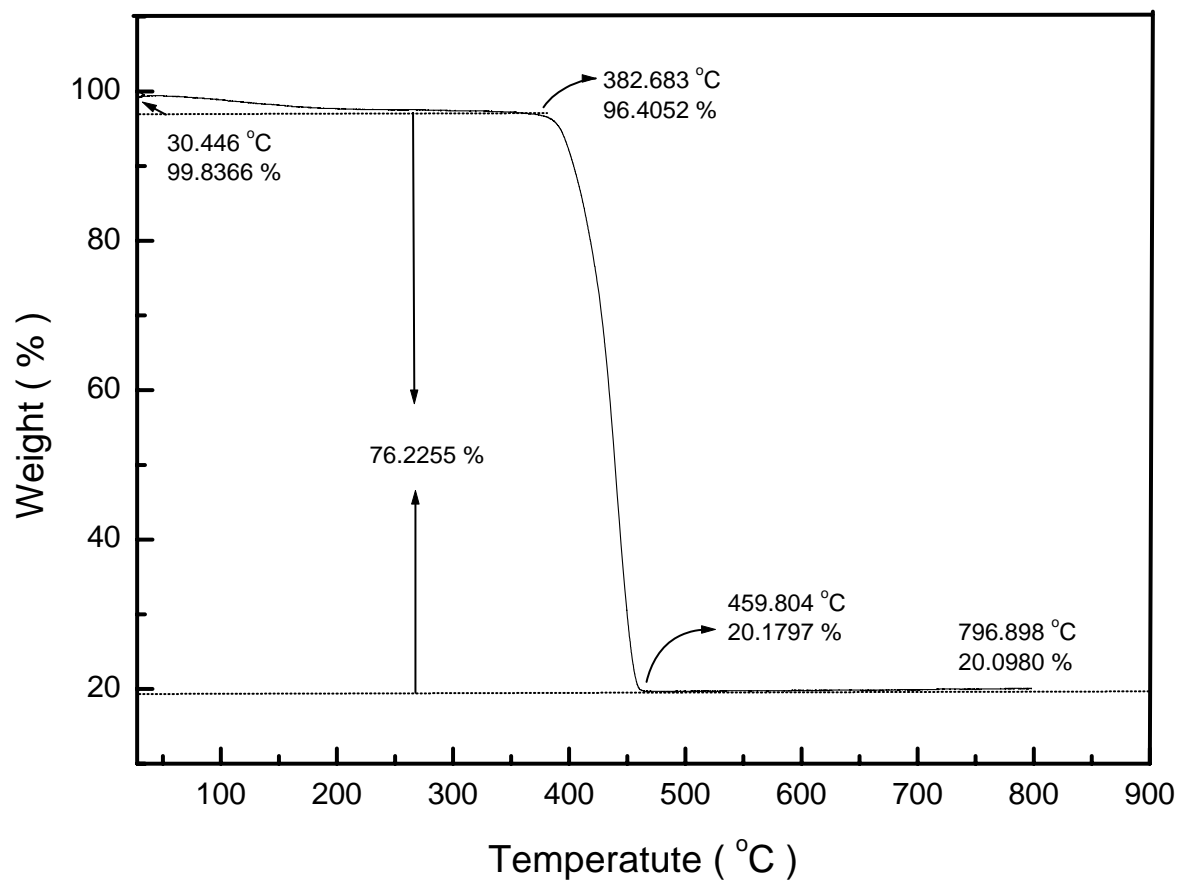


Figure S3

Figure S4