Supporting Information for:

**A Magnetic Ni-based Metal-Organic Framework with Interesting Transformation Dynamics**

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**S1. Chemical and thermal characterization of compounds.**

**Table S1.** Elemental analysis and TG/DTA curves of compound **1**.

|  |  |  |  |
| --- | --- | --- | --- |
| **{[Ni(μ-3isoani)2]·DMF}n (1)**  **C15H17NiN5O5 → M.W. = 406.26 g/mol** | | |  |
| **Ti–Tf** | **ΣΔm(%)** | **ΣΔm(%)theor** |
| 150-220 | 18.2 | 18.0 (–DMF) |
| 370-430 | 80.3 | 80.0 (-2 x 3isoani) |
| 410-800 | - | - (NiO) |
| **Elemental analysis**  Anal. Calc.: C, 44.37; H, 4.22; N, 17.25%. Found: C, 44.48; H, 4.09; N, 17.18%. | | |

**Table S2.** Elemental analysis and TG/DTA curves of compound **2**.

|  |  |  |  |
| --- | --- | --- | --- |
| **[Ni(3isoani)2(H2O)4] (2)**  **C12H18NiN4O8 → M.W. = 405.23 g/mol** | | |  |
| **Ti–Tf** | **ΣΔm(%)** | **ΣΔm(%)theor** |
| 120-160 | 17.8 | 17.8 (–4 x H2O) |
| 300-380 | 81.2 | 81.0 (-2 x 3isoani) |
| 380-800 | - | - (NiO) |
| **Elemental analysis**  Anal. Calc.: C, 35.59; H, 4.48; N, 13.83%. Found: C, 35.45; H, 4.39; N, 13.93%. | | |

**S2. FT-IR spectroscopy**

A description of FT-IR spectra and assignation of the main bands of compounds **1** and **2** is summarized. For compound **1**, in the high wavenumber region two bands are shown peaking at 3410 and 3300 cm-1 that correspond to the antisymmetric and symmetric stretching of the exocyclic amine group, respectively. Some weak bands are observed below 3000 cm-1, which are attributed to the symmetric and antisymmetric stretching vibrations between C-H of DMF molecules. The intense peak observed at 1680 cm-1 can be assigned to the stretching vibration of the carbonyl group of DMF molecules, whereas the bands observed in the region between 1620 and 1570 cm-1 appear as a result of the antisymmetric vibration of the carboxylate group of 3isoani ligand. Many intense bands appear in the 1500-1400 cm-1 region which are attributed to C-C and C-N vibrations of the aromatic ring of the ligand, while the symmetric stretching vibration of carboxylate groups occurs in the range of 1400-1200 cm-1. The remaining peaks at lower wavenumbers can be assigned to the distortions occurring in the aromatic ring and the carboxylate group of 3isoani ligand. The vibrations bands between M-O and M-N appear around 600 and 500 cm-1.

For compound **2**, a broad band covering the 3600-3000 cm-1 range are attributed to the coordinated water molecules. Moreover, some maxima are superimposed to the latter band peaking at 3440 and 3360 cm-1, which can be assigned to the antisymmetric and symmetric stretching of the exocyclic amine group, respectively. It is worth noticing that the absence of the band peaking at 1680 cm-1 assigned to C=O vibrations of DMF molecules, irrespective from the fact that the spectra is performed over fresh as-synthesized sample (direct preparation method) or on a sample coming from the transformed compound. Some intense bands appear in the 1660-1500 cm-1 region that correspond to the antisymmetric stretching vibrations of the carboxylate group of 3isoani, followed by the C-C and C-N vibrations of the aromatic ring of the ligand in the 1500-1400 cm-1 range. Symmetric vibrations of the carboxylate group are observed in the 1400-1200 cm-1 region. The resulting bands at lower wavenumbers are produced by the distortion of the aromatic ring and the carboxylate group of 3isoani ligand. Finally, M-O and M-N vibrations appear between 600-500 cm-1.



**Figure S** IR spectra of H3isoani and compounds **1** and **2**.

**S3. Powder X-ray diffraction analysis of as-synthesized compounds.**



**Figure S** Simulated and experimental PXRD of **1** with the full profile pattern matching analysis.



**Figure S** Comparison of the experimental PXRD of **2** with the simulated diffractogram of the Ni-based isostructural counterpart reported in reference [1]. Full profile pattern matching analysis of **2** is also shown as an inset.

**S4. Structural details of compounds 1 and 2.**

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**Figure S** View of the assembly of the building unit into the interpenetrated diamond-like framework of **1**. Note that its independent subnetwork is shown in a different colour.



**Figure S** View of the supramolecular network of **2** showing the hydrogen bonding network and π-π stacking interactions.

**Table S3.** Structural parameters (Å, º) of hydrogen bonds (Å, º) in compound **1**.a

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| *D–H...Ab* | *D–H* | *H...A* | *D...A* | *D–H...A* |
| N31A–H31A...O1A | 0.88 | 2.07 | 2.693(4) | 127.3 |
| N31A–H32A...O2A (i) | 0.88 | 2.11 | 2.919(4) | 152.9 |

a Symmetry codes: (i) –x+3/2, y+1/2, z-1/2 b D: donor. A: acceptor.

**Table S4.** CShMs for the coordination environment of the optimized fragments of compounds **1** and **2**. The lowest SHAPE values for each ion are shown highlighted indicating best fits. Note that this calculation for 2 has been performed over the optimized structure starting from X-ray coordinates of the isostructural Co(II) compound.

Codes:

|  |  |  |
| --- | --- | --- |
| HP-6 | 1 D6h | Hexagon |
| PPY-6 | 2 C5v | Pentagonal pyramid |
| OC-6 | 3 Oh | Octahedron |
| TPR-6 | 4 D3h | Trigonal prism |
| JPPY-6 | 5 C5v | Johnson pentagonal pyramid J12 |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Structure [ML6]** | **HP-6** | **PPY-6** | **OC-6** | **TPR-6** | **JPPY-6** |
| **1** | 26.916 | 24.439 | **3.157** | 13.953 | 28.420 |
| **2** | 31.981 | 29.448 | **0.097** | 16.415 | 32.732 |

**S5. dc magnetic susceptibility measurements.**



**Figure S** *χM-1 vs T* of **1** showing fitting of Curie-Weiss law in the 300-50 K range.



**Figure S** *χM-1 vs T* of **2** showing fitting of Curie-Weiss law.



**Figure S** Reduced magnetization curves in the 2-7 K and 1-7 T region for compound **1**.



**Figure** **S** Reduced magnetization curves in the 2-7 K and 1-7 T region for compound **2**.

**S6. DFT-Broken symmetry calculations on compound 1.**



**Figure S** Calculated spin density distributions for suitable dimeric models of high (S = 2) and low (S = 0) spin states of compound **1**.

**S7. CASSCF/NEVPT2/QPDT calculation results for compounds 1 and 2.**

**Table S5.** Calculated CAS(8,5)/NEVPT2 transition energies and SOC splitting of the ground state for the model complex of compound **1**.

|  |  |  |  |
| --- | --- | --- | --- |
| **Root** | **Multiplicity** | **∆E (cm-1)** | **∆ESOC (cm-1)** |
| 1 | 3 | 7001.3 | 0, 4.5, 4.7 |
| 2 | 3 | 10727.9 |  |
| 3 | 3 | 10921.8 |  |
| 0 | 1 | 13764.3 |  |
| 1 | 1 | 16008.3 |  |
| 5 | 3 | 16902.6 |  |
| 4 | 3 | 16929.8 |  |
| 6 | 3 | 18337.7 |  |
| 2 | 1 | 22703.9 |  |
| 3 | 1 | 25609.6 |  |
| 4 | 1 | 25825.5 |  |
| 7 | 3 | 27407.8 |  |
| 8 | 3 | 28599.7 |  |
| 5 | 1 | 29310.8 |  |
| 9 | 3 | 30436.6 |  |
| 7 | 1 | 31068.6 |  |
| 6 | 1 | 31113.2 |  |
| 8 | 1 | 34835.2 |  |
| 9 | 1 | 38439.3 |  |

**Table S6.** Calculated CAS(8,5)/NEVPT2 transition energies and SOC splitting of the ground state for the model complex of compound **2**.

|  |  |  |  |
| --- | --- | --- | --- |
| **Root** | **Multiplicity** | **∆E (cm-1)** | **∆ESOC (cm-1)** |
| 1 | 3 | 8548,6 | 0, 2.8, 22.5 |
| 2 | 3 | 10741,7 |  |
| 3 | 3 | 11962,2 |  |
| 4 | 3 | 14036,4 |  |
| 5 | 3 | 15098,8 |  |
| 6 | 3 | 15354,8 |  |
| 0 | 1 | 15898,4 |  |
| 1 | 1 | 16040,6 |  |
| 2 | 1 | 24026,4 |  |
| 3 | 1 | 24028,3 |  |
| 4 | 1 | 24468,7 |  |
| 7 | 3 | 26066,8 |  |
| 5 | 1 | 26435,7 |  |
| 8 | 3 | 26445,9 |  |
| 9 | 3 | 27089,1 |  |
| 6 | 1 | 29536,3 |  |
| 7 | 1 | 30152,4 |  |
| 8 | 1 | 30355,7 |  |
| 9 | 1 | 35860,4 |  |

**Table S7.** Individual contributions to *D* and *E* of the excited triplet and singlet states computed at the CAS(8,5)/NEVPT2 level for the model complex of compound **1**.

|  |  |  |  |
| --- | --- | --- | --- |
| **Root** | **Multiplicity** | ***D* (cm-1)** | ***E* (cm-1)** |
| 3 | 1 | -62.225 | 0.000 |
| 3 | 2 | 19.143 | -15.484 |
| 3 | 3 | 17.611 | 13.594 |
| 3 | 4 | 1.104 | 0.713 |
| 3 | 5 | 0.901 | -0.269 |
| 3 | 6 | 0.004 | 0.003 |
| 3 | 7 | 0.074 | 0.073 |
| 3 | 8 | 0.033 | -0.033 |
| 3 | 9 | 0.000 | 0.000 |
| 1 | 0 | 0.022 | 0.000 |
| 1 | 1 | 0.000 | 0.000 |
| 1 | 2 | 17.199 | 0.000 |
| 1 | 3 | -6.389 | 1.528 |
| 1 | 4 | -6.252 | -1.041 |
| 1 | 5 | 0.029 | 0.000 |
| 1 | 6 | -0.550 | -0.432 |
| 1 | 7 | -0.457 | 0.343 |
| 1 | 8 | 0.000 | 0.000 |
| 1 | 9 | 0.076 | 0.000 |

**Table S8.** Individual contributions to *D* and *E* of the excited triplet and singlet states computed at the CAS(8,5)/NEVPT2 level for the model complex of compound **2**.

|  |  |  |  |
| --- | --- | --- | --- |
| **Root** | **Multiplicity** | ***D* (cm-1)** | ***E* (cm-1)** |
| 3 | 1 | -6.725 | -20.309 |
| 3 | 2 | 35.050 | 35.050 |
| 3 | 3 | -22.656 | -14.578 |
| 3 | 4 | 0.005 | 0.005 |
| 3 | 5 | 0.006 | 0.006 |
| 3 | 6 | 0.037 | -0.045 |
| 3 | 7 | 0.000 | 0.000 |
| 3 | 8 | 0.001 | -0.002 |
| 3 | 9 | 0.000 | 0.000 |
| 1 | 0 | -0.002 | 0.003 |
| 1 | 1 | -0.001 | -0.001 |
| 1 | 2 | -7.544 | -7.544 |
| 1 | 3 | -6.685 | 7.270 |
| 1 | 4 | 14.216 | 0.266 |
| 1 | 5 | 0.011 | 0.001 |
| 1 | 6 | -0.023 | -0.023 |
| 1 | 7 | -0.006 | -0.006 |
| 1 | 8 | -0.060 | 0.060 |
| 1 | 9 | -0.002 | 0.009 |

|  |  |
| --- | --- |
|  |  |

**Figure S** Monomeric models of compounds **1** and **2** used for the computational calculations of the magnetic properties. Note that the model of compound **2** was optimized starting from the isostructural Co-based counterpart [2].

**S9. AC magnetic susceptibility measurements.**



**Figure S** *χM’* (circles) and *χM’’* (squares) vs *T* plots under *Hdc* = 1000 Oe for compound **2** at 10000 Hz of frequency for the oscillating field.



**Figure S** Optimization of the dc field for compound **1** in the form of τ vs H.



**Figure S** Cole-Cole plot for compound **1** showing the best fit for the selected temperature region.



**Figure S** Variable-temperature frequency dependence of the χM´´ signal of **1**.

**S10. References.**

1. Gantzler, N.; Kim, M.-B.; Robinson, A.; Terban, M.W.; Ghose, S.; Dinnebier, R.E.; York, A.H.; Tiana, D.; Simon, C.M.; Thallapally, P.K. Computation-informed optimization of Ni(PyC)2 functionalization for noble gas separations. *Cell Reports Phys. Sci.* **2022**, *3*, 101025, doi:https://doi.org/10.1016/j.xcrp.2022.101025.

2. Pajuelo-Corral, O.; Pérez-Yáñez, S.; Vitorica-Yrezabal, I.J.; Beobide, G.; Zabala-Lekuona, A.; Rodríguez-Diéguez, A.; Seco, J.M.; Cepeda, J. A metal-organic framework based on Co(II) and 3-aminoisonicotinate showing specific and reversible colourimetric response to solvent exchange with variable magnet behaviour. *Mater. Today Chem.* **2022**, *24*, 100794, doi:https://doi.org/10.1016/j.mtchem.2022.100794.