

Supplementary Information

Selective Adsorption of Dihydrogen Isotopes on DUT-8 (Ni,Co) Monitored by *In Situ* Electron Paramagnetic Resonance

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S1. Supplementary Information

Table S11. The contribution of two different species in percentage (Species A and Species B) obtained by spectral simulation for the CW-EPR spectra at each pressure point during desorption stage of D₂ from the DUT-8(Ni_{0.98}Co_{0.02}).

| D ₂ Pressures / mbar | Rhombic Species A / % | Axial Species B / % |
|---------------------------------|-----------------------|---------------------|
| 644 | 100 | 0 |
| 558 | 100 | 0 |
| 265 | 100 | 0 |
| 90 | 100 | 0 |
| 57 | 80 | 20 |
| 35 | 65 | 35 |
| 15 | 35 | 65 |
| 1.25 | 0 | 100 |
| 0.001 | 0 | 100 |

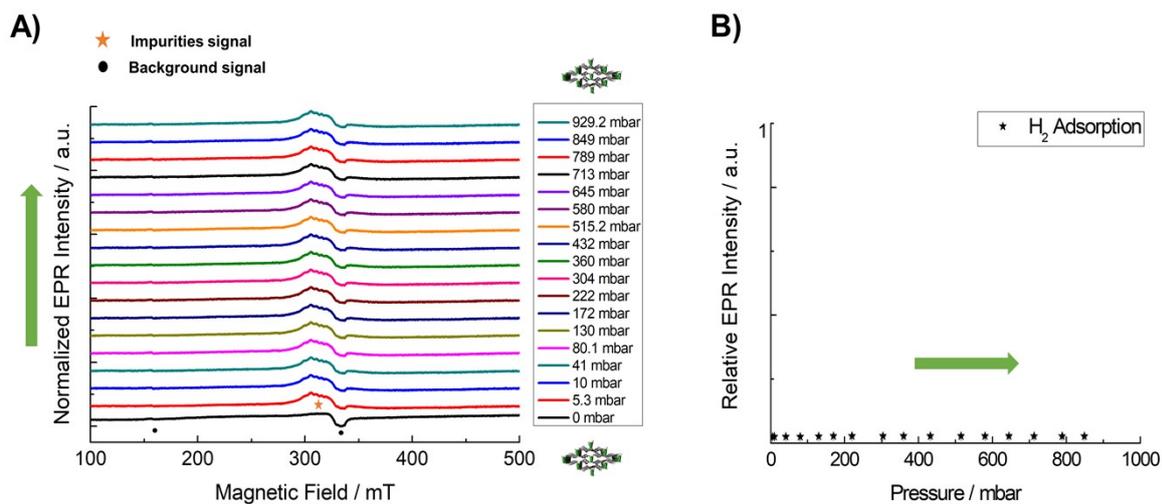


Figure S11. A) CW-EPR spectra of DUT-8(Ni_{0.98}Co_{0.02}) in response to H₂ adsorption recorded *in situ* from $p = 0.001$ mbar to $p = 929.2$ mbar at $T = 19.5$ K. B) plot of EPR signal intensity for DUT-8(Ni_{0.98}Co_{0.02}) normalized with the highest EPR intensity for D₂ gas during adsorption stage. Green arrows guide the eye for the increasing of pressure.

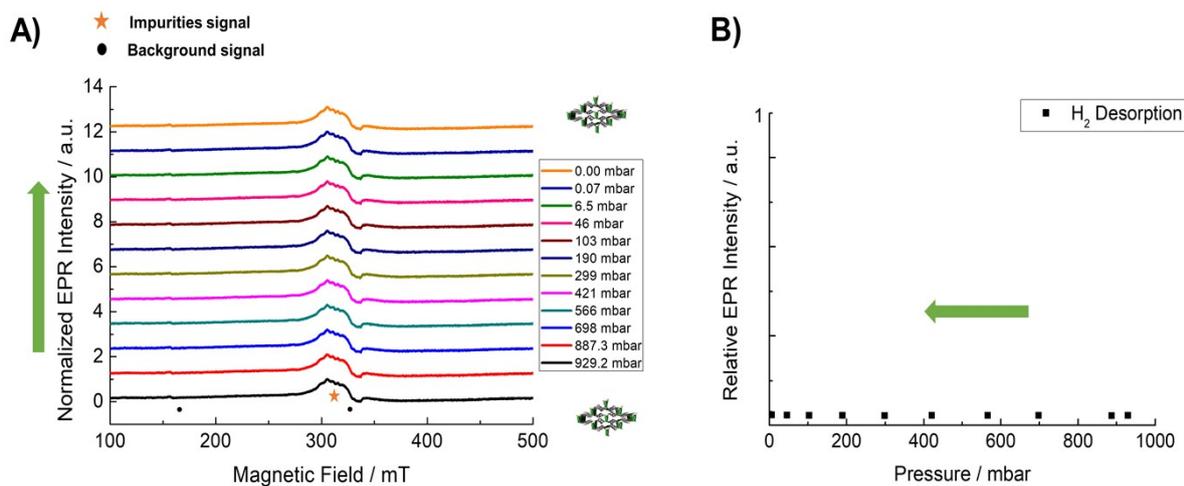


Figure S12. A) CW-EPR spectra of DUT-8(Ni_{0.98}Co_{0.02}) in response to H₂ desorption recorded *in situ* from $p = 929.2$ mbar to $p = 0.001$ mbar at $T = 19.5$ K. B) plot of EPR signal intensity for DUT-8(Ni_{0.98}Co_{0.02}) normalized with the highest EPR intensity for D₂ gas during adsorption stage. Green arrows guide the eye for the decreasing pressure.

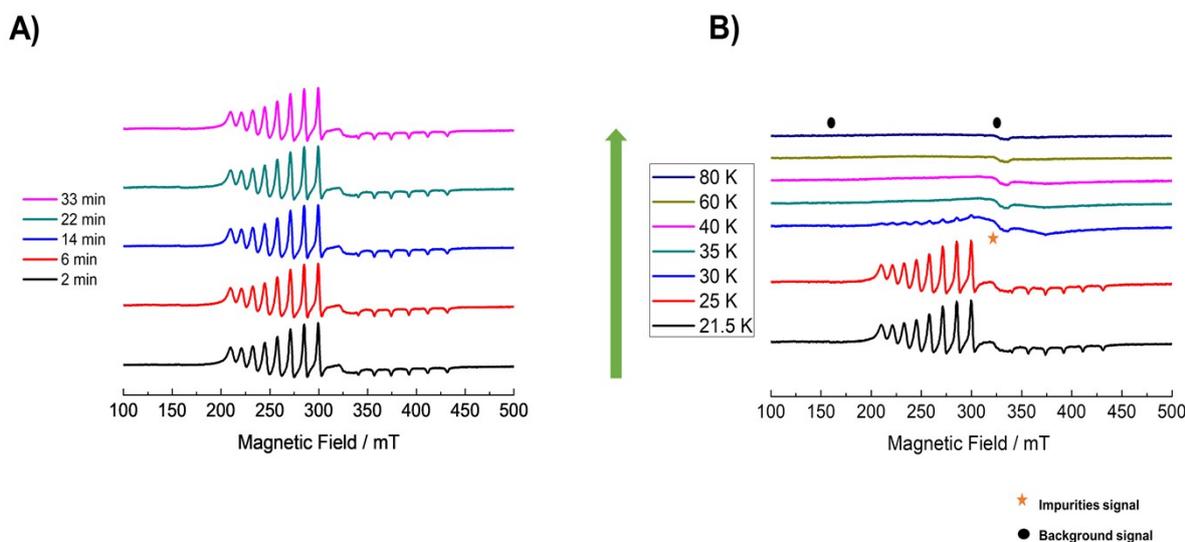


Figure S13. A) CW-EPR spectra of DUT-8(Ni_{0.98}Co_{0.02}) in response to D₂ desorption recorded *in situ* from $t = 2$ min to $t = 33$ min at $p = 0.001$ mbar and $T = 21.5$ K. B) CW-EPR spectra of DUT-8(Ni_{0.98}Co_{0.02}) with variation of desorption temperature at fixed $p = 0.001$ mbar.

S2. Materials and Methods

S2.1 Sample Preparation

The mixed-metal DUT-8(Ni_{0.98}Co_{0.02}) was synthesized according to Ehrling and co-workers¹ by preparing the metal ion sources from the following solutions: Co(NO₃)₂·6H₂O (75 mg, 0.028 mmol) and Ni(NO₃)₂·6H₂O (399.6 mg, 1.372 mmol) were dissolved in 3 ml DMF for each metal ion solution. The linker was prepared by dissolving 2,6-H₂ndc (303.4 mg, 1.4 mmol) in 15 ml DMF, and the pillaring agent, dabco (100 mg, 0.9 mmol) was dissolved in 9 ml MeOH. All four separate solutions were combined in a Teflon vessel and heated in an autoclave up to 393 K followed by annealing for 48 h. The resulting products were washed several times with fresh DMF and exchanged with DCM under ambient conditions. The DUT-8 (Ni_{0.98}Co_{0.02}) powder in DCM was placed inside the EPR quartz tube with 3.8 mm inner diameter. Evacuation of DCM was performed at room temperature for 24 h prior to the dihydrogen isotopes adsorption-desorption experiments.

S2.2 In situ CW-EPR experiments

The *in situ* CW-EPR experiments were performed with a Bruker EMX micro (X-band, 9.4 GHz) spectrometer fitted with an ER 4119 HS cylindrical cavity. For low-temperature experiments at $T = 19$ - 23 K, an Oxford Instruments He cryostat ESR 900 was used. Spectral simulations of the EPR spectra were performed using the MATLAB simulation package EasySpin². Both H₂ and D₂ gas with 99.999% purity was purchased from Linde AG. A home-built gas loading line was previously introduced by Mendt and co-workers³. This gas manifold setup provides an exposure of H₂ and D₂ gas to the sample at a defined pressure and temperature, while the sample is kept in the cryostat of EPR spectrometer. In the present work, the H₂ and D₂ pressure was increased stepwise, starting at a pressure of $p = 0.001$ mbar until the saturated vapor pressure p_0 was reached at target temperature. Then, the pressure was gradually decreased down to $p = 0.001$ mbar again for the desorption stage. In most cases, at each pressure, EPR spectra were measured every 10 min approximately or until no spectral changes were observed anymore.

S3. Evaluation of EPR signal that corresponds to the Co²⁺-Ni²⁺ paddle wheels

We would like to highlight some key points from the previous literatures^{1,4} for a thorough analysis of the Co²⁺-Ni²⁺ adduct nature. As a comparison, previous EPR study of Cu²⁺ doped DUT-8 (Ni_{0.98} Cu_{0.02}) strongly indicates the ferromagnetic coupling between Ni²⁺-Cu²⁺ mixed metal units where Ni²⁺ ion behave as S = 1 high spin state. Since it is reasonable that the strength and symmetry of the ligand field at the Ni²⁺ ion in the mixed-metal unit does not change drastically if one exchanges the neighbouring Cu²⁺ by a Co²⁺ ion, we expect that the Ni²⁺ is also in a similar spin state (S = 1). Ultimately, the most possible assignment in the case of mixed Co²⁺-Ni²⁺ unit is an antiferromagnetic coupling between high spin of Co²⁺ (S = 3/2) and Ni²⁺ (S = 1) with S_{eff} = 1/2 within the limit of strong isotropic exchange scenario. The interpretation of the signal based on a simple-spin Hamiltonian approach is not appropriate since the ground state of the high spin Co²⁺ ion can be orbitally degenerated, and one might have to include the orbital momentum in the Hamiltonian describing the magnetic coupling between Co²⁺ and Ni²⁺ ions. Kahn and co-workers⁵ proposed a description of the interaction between orbitally degenerate ground states, which includes different exchange terms according to the different orbital terms involved. This consequently increases the number of magnetic parameters significantly which prevents a fundamental understanding of the coupling between Co²⁺ and Ni²⁺ ions without knowing the single ion Hamiltonian. For these reasons, an analysis of the contribution of the Co²⁺ d orbital to the wavefunction of the S = 1 state of the magnetically coupled Co²⁺-Ni²⁺ pair appears to be very difficult and presumably highly speculative. We have not found any discussion in the literature about the influence of the orbital degeneracy on the hyperfine interaction in case of magnetically coupled ion pair. However, the fact that the effective g-tensor principal values in our case is in the vicinity of 2 excluded the possibility of having ferromagnetic coupling (Otherwise, at least one effective g-tensor principal value should be larger than four) as it was observed by Banci and co-workers⁶ for Co²⁺-Ni²⁺ pairs in dinuclear triketonate complexes. In addition, we observed the ⁵⁹Co hfi which is three times smaller than the value expected⁷ for the monomeric low spin Co²⁺ (typically smaller than 1000 MHz). Therefore, we concluded that the observed EPR signal of the Co²⁺-Ni²⁺ paddle wheel units are caused by the magnetically coupled states of the ion pair and, consequently the orbitals of both ions of the pair are involved in the electronic wavefunction of the observed spin state.

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