SUPPORTING INFORMATION

Structural Transitions of the Metal-Organic Framework DUT-49(Cu) upon Physi- and Chemisorption Studied by in situ EPR Spectroscopy

Daniil M. Polyukhov, a Simon Krause, b Volodymyr Bon, b Artem S. Poryvaev, a,c,d Stefan Kaskel, b,* Matvey V. Fedin a,c,*

a International Tomography Center SB RAS, Novosibirsk, 630090, Russia
b Chair of Inorganic Chemistry I, Technische Universität Dresden, Bergstraße 66, 01069, Dresden
c Novosibirsk State University, Novosibirsk, 630090, Russia
d N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Novosibirsk, 630090, Russia

mfedin@tomo.nsc.ru, stefan.kaskel@tu-dresden.de

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1. Experimental Details

**Synthesis.** The synthesis of the ligand and DUT-49(Cu) was performed using the procedure reported previously.\textsuperscript{S1} The phase purity was confirmed by PXRD, crystallite size distribution in the sample by SEM and textural properties and stimuli-induced flexibility by nitrogen adsorption at 77 K reported in Ref.S1.

**EPR details.** EPR studies were performed using Bruker EMX X-band EPR and Bruker Elexsys E580 X/Q-band EPR spectrometers, both equipped with Oxford Instruments temperature control systems (T=4-300 K). The EMX spectrometer also had a home-made gas sorption setup (scheme presented in Supporting Information, SI). Continuous wave (CW) EPR spectra were recorded at conditions avoiding undesired modulation broadening and microwave (mw) saturation. For all simulations EasySpin toolbox for Matlab was used.\textsuperscript{S2}

In all cases, powdered desolvated DUT-49(Cu) samples were placed into the quartz sample tubes (OD = 2.8 mm and 3.8 mm) under inert atmosphere and sealed off at vacuum or connected and used at the gas sorption setup. The sorption setup allowed carrying out a CW EPR study with \textit{in situ} gas sorption. It included the calibration (fixed) volume and turbomolecular pump for sample evacuation, as well as necessary valves and fittings to provide high isolation. The sorption setup was connected to the sample tube placed in the EPR resonator via PTFE tube (OD = 6 mm). This setup was used to evacuate or add gases directly into the sample tube. It was possible to control pressure in the range from $10^{-2}$ to $10^{3}$ mbar. Simultaneously, the cryosystem could be used when necessary. The scheme of setup is provided below in Section 4 of Supporting Information.

**Sorption experiments.** Sorption experiments were performed using volumetric technique on BELSORP-max (MICROTRAC MRB) instrument. Helium gas of 99.999% purity was used for determination of the dead volume of the measurement cells before the measurement. \textit{n}-Butane gas of 99.99% purity and anhydrous diethyl ether (Sigma Aldrich >99.7%) was used in sorption experiments. Temperature of 298 K (\textit{n}-butane and diethyl ether sorption) and 273 K (\textit{n}-butane physisorption) was ensured by 2-propanol-filled Julabo F25-HE thermostat, connected to the thermostatic bath. In the case of \textit{n}-butane, the physisorption measurements were conducted in the pressure range 0.025 – 966 mbar using adsorption equilibrium conditions of 1% of pressure change within 400 s. In the case of diethyl ether, 0.23 – 679 mbar pressure range was covered in adsorption branch and adsorption equilibrium conditions of 0.3% pressure change within 500 s was used. In all adsorption experiments 10 – 25 mg of DUT-49 sample was used.
2. Auxiliary EPR data and simulations

EPR spectra of all states found in course of our experiments with DUT-49(Cu) (op, cp, re-op, cp*, op* at high/low pressure) were simulated (Fig.S1, Fig.S2).

**Figure S1.** X-band EPR spectra of DUT-49(Cu) at 9.9 GHz (a) and 9.4 GHz (b). Red lines show simulations. See Table S1 for parameters.

**Figure S2.** High-field component of X-band EPR spectra of DUT-49(Cu) at 9.9 GHz for samples (from bottom to top): activated, op* under ~25 mbar of diethyl ether, cp*, oP* under ~660 mbar of diethyl ether.

Table S1 shows the principal parameters of simulation, the most crucial of which are $D$ value ($E=0$ in all cases), g-tensor and $A_{zz}$ component of A-tensor.
Table S1. Parameters of simulation for the data shown in Figs. S1 and S2. $D_{\text{dip}}$ (calculated) is obtained based on point dipole approximation and EXAFS data.

| Sample                      | g-factor         | $A_{zz}$ / MHz | $D$ / mT | $D_{\text{dip}}$ calculated / mT |
|-----------------------------|------------------|----------------|----------|---------------------------------|
| $op$ (activated, bare)      | [2.042 2.042 2.295] | 250-265        | 318.0 (±0.3) | 225                             |
| $cp$ (n-butane)             | [2.060 2.060 2.295] | 210 (±15)      | 320.6 (±0.3) | 223                             |
| $op$ (n-butane, = re-$op$)  | [2.050 2.050 2.295] | 240 (±15)      | 315.5 (±0.3) | 221                             |
| $op^*$ (Et$_2$O, low pressure) | [2.052 2.052 2.310] | 190 (±15)      | 331.3 (±0.3) | -                               |
| $cp^*$ (Et$_2$O)            | [2.060 2.062 2.340] | 160 (±15)      | 341.5 (±0.3) | -                               |
| $op^*$ (Et$_2$O, high pressure) | [2.062 2.062 2.340] | 190 (±15)      | 337.5 (±0.3) | -                               |

Figure S3 shows the EPR-detected adsorption of $n$-butane at 293 K, which is an additional data similar to those shown in Figure 3 of the main text for 298 K and 273 K.

![Figure S3](image-url)

Figure S3. X-band CW EPR spectra of DUT-49(Cu) as a function of the applied pressure of $n$-butane (values indicated on the right) at 290-293 K. Microwave frequency $v_{\text{mic}}$=9.39 GHz. The sample was activated (kept for 12 h under $10^{-3}$ mbar at 423 K) prior to measurement. Color dotted lines guide the eye for spectral transformations. Blue shading corresponds to the initial (after activation) $op$ state, red – to $cp$ state, green – to reopened $op$ state (re-$op$) at high pressure of $n$-butane.

It is useful for visualization to simultaneously plot the EPR-derived map of structural states and the data of adsorption isotherms (Figure S4). The data of EPR and adsorption isotherms agree well in all cases, except for the point $p/p_0=0.4$ in Figure S4a for $T=273$ K. Figure S4b ($T=298$ K) shows that $cp$ state maintains up to $p/p_0=0.4$, and Figure S3 ($T=293$ K) indicates that $cp\rightarrow re-op$ transition occurs between $p/p_0=0.4$ and $p/p_0=0.45$. Therefore, we believe that $p/p_0=0.4$ lies on the border between two states, and small fluctuations of temperature (~2-3 K) can lead to the predominance of either state. The values $p/p_0=0.45-0.5$ are already close to the onset of $cp\rightarrow re-op$ transition manifested by sorption isotherms.
Figure S4. (bottom panels) Sorption isotherms shown in Figs. 2 and 4a: n-butane at 273 K (a), n-butane at 298 K (b), Et₂O at 298 K (c). (top panel) Corresponding maps of the structural states (op, cp, re-op) derived from EPR spectra vs. supplied pressure shown in Figures 3 and 4b. Circles show actual measurements, and lines guide the eye.

In general, the results shown in Figures 2-4 of the main text and additional/expanded Figures S3-S4 of Supporting Information indicate good correlations between EPR and sorption isotherms.
3. Interpretation of the obtained D values

As was mentioned in the main text of the paper, the apparent D value has two contributions:

$$D_{\text{dip}} = -\frac{2g_z^2+(g_x^2+g_y^2)/2}{2r_{\text{Cu-Cu}}^3} \beta^2; \quad D_{\text{ex}} = \left(\frac{\Delta g}{g}\right)^2 J,$$

where $g_{x,y,z}$ are the components of g-tensor, $\Delta g$ is characteristic deviation of $g_i$ values, $g = (g_x + g_y + g_z)/3$, $r_{\text{Cu-Cu}}$ is the distance between two copper ions, and $J$ is the isotropic exchange interaction between two copper ions. As was mentioned in the text, the contributions of $D_{\text{dip}}$ and $D_{\text{ex}}$ are comparable in our case (see also Table S1). When geometry of the dimer changes, these two contributions might change in opposite directions. For instance, the $\text{op} \rightarrow \text{cp}$ transition upon adsorption of n-butane leads to a slight lengthening of $r_{\text{Cu-Cu}}$ and thus to a decrease of $D_{\text{dip}}$. This is opposite to the experimental observations, showing that $D$ increases from 318 mT to 320.6 mT. Therefore, the observed increase of $D$ should be assigned to the term $D_{\text{ex}}$. Based on this clear case, where $r_{\text{Cu-Cu}}$ values are known for $\text{op}$ and $\text{cp}$ states (in fact, they were measured upon methane adsorption, S1 but are safely assumed to be similar to the case of n-butane adsorption), we assume that in general the changes in $D_{\text{ex}}$ govern all observed changes of $D$.

The dependence of $D_{\text{ex}}$ term on the structure of dimer is not obvious, and, generally, requires detailed theoretical studies. However, as this is not the main purpose of our work, we limit ourselves only to the qualitative correlations that allow us to understand the trends in $D$ observed in experiment.

The components of g-tensor enter into both $D_{\text{dip}}$ and $D_{\text{ex}}$ terms, and experimentally observed increase of $g_z$ upon Et$_2$O adsorption should lead to increase of the both terms. However, since $D_{\text{ex}}$ term is proportional to the square of $\Delta g/g$, we assume that it plays major role in the observed changes of $D$. Therefore, we plotted the experimentally observed $D$ values vs. $(\Delta g/g)^2$ in Figure S5.
Figure S5. Dependence of experimental $D$ parameter on experimental $(\Delta g/g)^2$.

A reasonably good correlation is observed for $op$ (bare), $op^*$ (Et$_2$O, low pressure), $op^*$ (Et$_2$O, high pressure) and $cp^*$ (Et$_2$O) states. This means that when noticeable changes in $g_z$ are observed, the main factor contributing to the changes of $D$ is the anisotropic exchange interaction. Regarding the sorption of $n$-butane, the changes of $g_z$ are small, and we likely observe an interplay between $D_{\text{dip}}$ and $D_{\text{ex}}$ terms, resulting in the outliers in Figure S5.

Overall, the observed changes in $D$ values upon physisorption of $n$-butane and chemisorption of Et$_2$O are found to be quite reasonable.
4. Supplementary adsorption data

Figure S6 shows the dependence of number of adsorbed molecules of \( n \)-butane and diethyl ether per copper paddle-wheel unit vs. \( p/p_0 \). Evidently, diethyl ether starts to adsorb at lower \( p/p_0 \) reaching the value of 1.25 molecules / PW at \( p/p_0 = 0.0015 \). This is an indication of stronger interaction in case of diethyl ether compared to \( n \)-butane. The isotherms were measured at different temperatures in order to record adsorbed amounts up to \( p/p_0=1 \). However, diethyl ether was measured at higher temperature, therefore the conclusion on stronger interaction in this case is even more reliable.

![Figure S6](image)

**Figure S6.** Dependence of adsorbed amount of \( n \)-butane (T=273 K) and diethyl ether (T=298 K) vs. \( p/p_0 \).

These results, obtained via the adsorption isotherms analysis, strengthen furthermore the results obtained by EPR (namely, the analysis of zero-field splitting, g-tensor and kinetic desorption behavior), as well as visual color indication of chemisorption (inset to Fig.4a). Altogether, these results provide undoubted evidence of the chemisorption in case of diethyl ether vs. physisorption in case of \( n \)-butane.
5. Scheme of the sorption setup

Figure S7. The homemade gas sorption setup was used in the EPR study. The total dead volume of the system is ~20 ml. Bypass line provides high vacuum directly to sample line. Gas source line supplies the sample with vapor of adsorptive via limited volume equipped with a pressure gauge (1 – 1600 mbar).
6. References

(S1) Többens, D. M.; Pillai, R. S.; Wallacher, D.; Senkovska, I.; Kaskel, S.; Bon, V.; Krause, S.; Maurin, G. The Effect of Crystallite Size on Pressure Amplification in Switchable Porous Solids. *Nat. Commun.* **2018**, *9*, 1573.

(S2) Stoll, S.; Schweiger, A. EasySpin, a Comprehensive Software Package for Spectral Simulation and Analysis in EPR. *J. Magn. Reson.* **2006**, *178*, 42–55.