## Supporting Information

# Hydroxide Bridged Cubane Complexes of Nickel(II) and Cadmium(II): Magnetic, EPR and Unusual Dynamic Properties 

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Saturation Transfer Experiment. During the saturation transfer experiments we saturate the signal of one of the exchanging protons and follow the decrease in the intensity of the other resonance as a function of saturation time (the saturation time is increased with 0.25 seconds until the intensity of the second resonance remains constant). The natural logarithm of this decrease in intensity is proportional to the rate constant $(k)$. To obtain good results through better separation of exchanging resonances, the sample was cooled to $0^{\circ} \mathrm{C}$.

According to Fors $\square \mathrm{n}$, Hoffman ${ }^{\text {S1 }}$ and Babailov papers ${ }^{\text {S2 }}$ we have plotted the values of $\ln \left(I_{\mathrm{i}}-I_{\infty}\right)$ against the saturation time $(t)$, as seen on Figure 9 , where $I_{\mathrm{i}}$ is the residual intensity of the exchanging resonance after intermediate amounts of saturation times and $I_{\infty}$ is the residual intensity of the exchanging resonance after complete saturation. The slope of this straight line gives $-\left(1 / \tau_{1 \mathrm{a}}\right)$, where $\tau_{1 \mathrm{a}}$ is the overall lifetime of the process, which includes the spin-lattice relaxation time $\left(T_{1 \mathrm{a}}\right)$ and the lifetime of the exchanging resonance at the other site $\left(\tau_{\mathrm{a}}\right)$. Standard inversion recovery experiment results in values of $T_{1 \mathrm{a}}$. Substitution of the known values in the equation below (Scheme S1) $1 / \tau_{\mathrm{a}}$ was calculated, which equals to $k$ if the equilibrium is first order. The $\Delta G^{\ddagger}$ was calculated by applying the Eyring equation to $k$.

$$
\begin{align*}
& \frac{1}{\tau_{1 a}}=\frac{1}{\tau_{\mathrm{a}}}+\frac{1}{T_{1 \mathrm{a}}}  \tag{4}\\
& k=\frac{1}{\tau_{a}} \tag{5}
\end{align*}
$$

Scheme S1.

Table S1. Ni-O-Ni bond angles for $\mathbf{1}(\AA)$.

| $\mathrm{Ni}(1)-\mathrm{O}(1)-\mathrm{Ni}(2)$ | $99.20(13)$ |
| :--- | :--- |
| $\mathrm{Ni}(1)-\mathrm{O}(1)-\mathrm{Ni}(3)$ | $100.82(13)$ |
| $\mathrm{Ni}(1)-\mathrm{O}(2)-\mathrm{Ni}(2)$ | $97.93(13)$ |
| $\mathrm{Ni}(1)-\mathrm{O}(3)-\mathrm{Ni}(4)$ | $100.51(13)$ |
| $\mathrm{Ni}(2)-\mathrm{O}(4)-\mathrm{Ni}(3)$ | $100.30(13)$ |
| $\mathrm{Ni}(2)-\mathrm{O}(1)-\mathrm{Ni}(3)$ | $100.56(13)$ |
| $\mathrm{Ni}(2)-\mathrm{O}(4)-\mathrm{Ni}(4)$ | $98.82(13)$ |
| $\mathrm{Ni}(3)-\mathrm{O}(3)-\mathrm{Ni}(1)$ | $101.46(13)$ |
| $\mathrm{Ni}(3)-\mathrm{O}(3)-\mathrm{Ni}(4)$ | $99.45(13)$ |
| $\mathrm{Ni}(3)-\mathrm{O}(4)-\mathrm{Ni}(4)$ | $98.16(13)$ |
| $\mathrm{Ni}(4)-\mathrm{O}(2)-\mathrm{Ni}(1)$ | $100.31(13)$ |
| $\mathrm{Ni}(4)-\mathrm{O}(2)-\mathrm{Ni}(2)$ | $98.45(13)$ |

Table S2. Ni-O-Ni bond angles for $2(\AA)$.
$\mathrm{Ni}(1)-\mathrm{O}(1)-\mathrm{Ni}(1) \quad 101.44(11)$
$\mathrm{Ni}(1)-\mathrm{O}(1)-\mathrm{Ni}(2) \quad 98.20(11)$
$\mathrm{Ni}(1)-\mathrm{O}(2)-\mathrm{Ni}(2) \quad 98.06(11)$
$\mathrm{Ni}(1)$ ' $-\mathrm{O}(1)-\mathrm{Ni}(2) \quad 100.69(12)$
$\mathrm{Ni}(2){ }^{\prime}-\mathrm{O}(2)-\mathrm{Ni}(1) \quad 101.23(12)$
$\mathrm{Ni}(2){ }^{\prime}-\mathrm{O}(2)-\mathrm{Ni}(2) \quad 98.21(12)$


Figure S1. Frequency dependencies of the prominent resonances in the 30 K spectra of 1. Horizontal axis: frequency in GHz. Vertical axis: magnetic induction in Tesla. Circles: experimental; dots: calculated. Fitting these dependencies allowed to find the spin Hamiltonian parameters for the ground spin state $S=4$ which were subsequently used to simulate the powder EPR spectra.



Figure S2. Energy levels in magnetic field calculated for $\mathrm{S}=4$ with $g_{\mathrm{x}}=2.205, g_{\mathrm{y}}=2.157, g_{\mathrm{z}}=$ 2.204, $D=-0.299 \mathrm{~cm}^{-1}, E=-0.036 \mathrm{~cm}^{-1}, B_{4}{ }^{0}=-3.7 \cdot 10^{-5} \mathrm{~cm}^{-1}, B_{4}{ }^{2}=4.2 \cdot 10^{-4} \mathrm{~cm}^{-1}, B_{4}{ }^{4}=-1.6 \cdot 10^{-4}$ $\mathrm{cm}^{-1}$. The magnetic field on the horizontal axis is given in Gauss and the energy on the vertical axis is in $\mathrm{cm}^{-1}$. The vertical red lines represent the 328.8 GHz microwave quantum energy. With $D$ negative, the lowest-field $\Delta M_{\mathrm{S}}=1$ transition $(85500 \mathrm{G})$ at the molecular Z orientation starts from the lowest energy state and is therefore observed at 3 K , while next transitions at that orientation are suppressed, but emerge at higher temperatures when next levels become populated. At the X and Y orientations, the highest-field transitions start from the lowest energy level and are observed at 3 K . The thermal energy, kT , at 3 K is $2.1 \mathrm{~cm}^{-1}$, less than the 328.8 GHz microwave quantum energy of $10.96 \mathrm{~cm}^{-1}$. These relations would be inverted if $D, E$ were positive, resulting in incorrect EPR simulation (Figure S4).


Figure S3. EPR spectrum of 1 at $30 \mathrm{~K}, 222.4 \mathrm{GHz}$ and a simulation with $S=4$ with with $g_{\mathrm{x}}=$ 2.205, $g_{\mathrm{y}}=2.157, g_{\mathrm{z}}=2.204, D=-0.299 \mathrm{~cm}^{-1}, E=-0.036 \mathrm{~cm}^{-1}, B_{4}{ }^{0}=-3.7 \cdot 10^{-5} \mathrm{~cm}^{-1}, B_{4}{ }^{2}=$ $4.2 \cdot 10^{-4} \mathrm{~cm}^{-1}, B_{4}{ }^{4}=-1.6 \cdot 10^{-4} \mathrm{~cm}^{-1}$ (see the main text).


Figure S4. EPR ( $3 \mathrm{~K}, 328.8 \mathrm{GHz}$ ) spectrum of 1 and a simulation with the signs of all zfs parameters ( $D, E, B_{4}{ }^{i}$ ) inverted. Compare to the simulation using correct signs in the main text.


Figure S5. The four Singly Occupied Molecular Orbitals (SOMOs) for the interacting pair Ni1Ni2.

## References

(S1) Forsén, S.; Hoffman, R. A. J. Chem. Phys. 1963, 39, 2892.
(S2) Babailov, S. P.; Krieger, Y. G. J. Struct. Chem. 2001, 42, 305.

