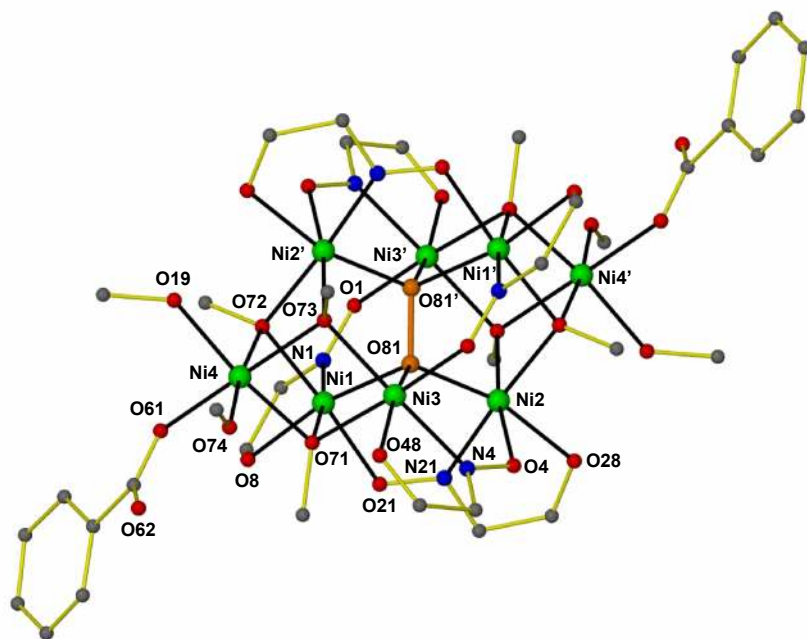
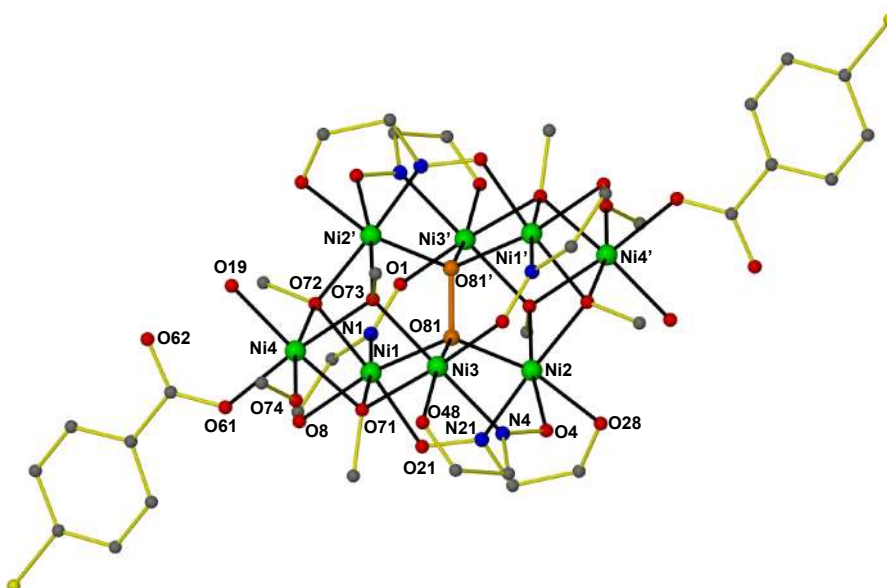


## A family of [Ni<sub>8</sub>] cages templated by $\mu_6$ -peroxide from dioxygen activation

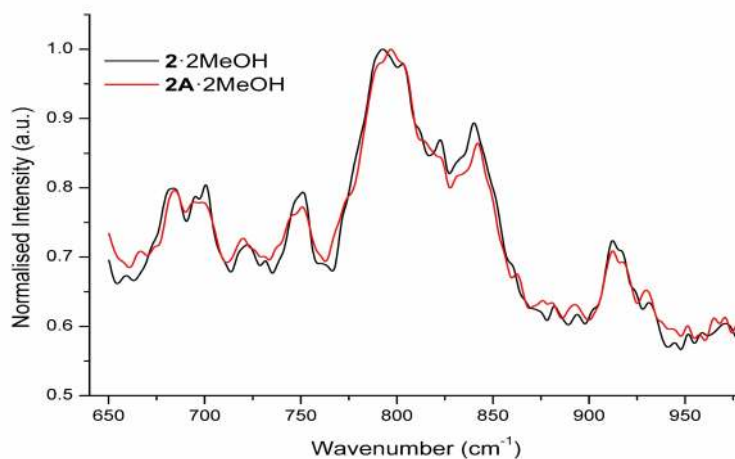
Alexandros Perivolaris, Constantinos C. Stoumpos, Jolanta Karpinska, Alan G. Ryder, Jamie M. Frost, Kevin Mason, Alessandro Prescimone, Alexandra M. Z. Slawin, Vadim G. Kessler, Jennifer S. Mathieson, Leroy Cronin, Euan K. Brechin\* and Giannis S. Papaefstathiou\*



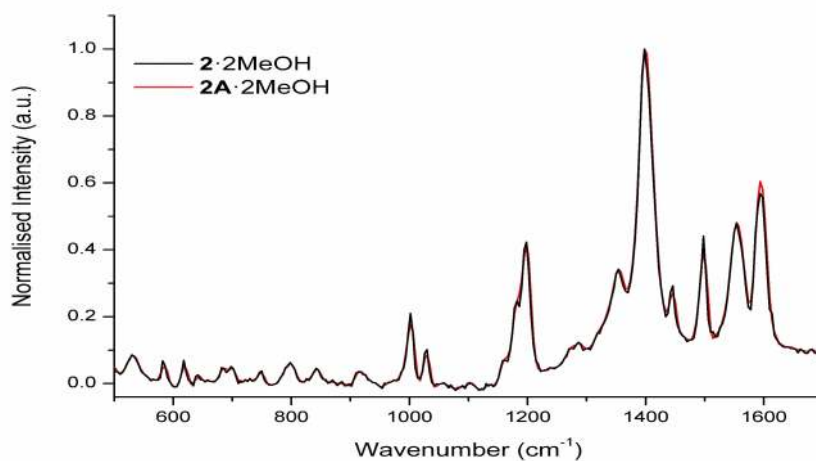
**Fig. S1.** The structure of [Ni<sub>8</sub>(O<sub>2</sub>)(abmo)<sub>6</sub>(PhCO<sub>2</sub>)<sub>2</sub>(MeO)<sub>6</sub>(MeOH)<sub>4</sub>] **2**. All hydrogen atoms and most carbon atoms have been omitted for clarity. Color code: Ni green, C grey, N blue, O red. The  $\eta^3:\eta^3:\mu_6$ -O<sub>2</sub><sup>2-</sup> has been highlighted in orange. Symmetry code: (') 1-x, 1-y, 2-z.



**Fig. S2.** The structure of [Ni<sub>8</sub>(O<sub>2</sub>)(abmo)<sub>6</sub>(4ClPhCO<sub>2</sub>)<sub>2</sub>(MeO)<sub>6</sub>(MeOH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] **3**. All hydrogen atoms and most carbon atoms have been omitted for clarity. Color code: Ni green, C grey, N blue, O red, Cl yellow. The  $\eta^3:\eta^3:\mu_6$ -O<sub>2</sub><sup>2-</sup> has been highlighted in orange. Symmetry code: (') -x, 1-y, 1-z.



**Fig. S3.** Overlaid normalized Raman spectra of  $[\text{Ni}_8(\text{O}_2)(\text{abmo})_6(\text{PhCO}_2)_2(\text{MeO})_6(\text{MeOH})_4] \cdot 2\text{MeOH}$  ( $2 \cdot 2\text{MeOH}$ ) and  $[\text{Ni}_8(^{18}\text{O}_2)(\text{abmo})_6(\text{PhCO}_2)_2(\text{MeO})_6(\text{MeOH})_4] \cdot 2\text{MeOH}$  ( $2\text{A} \cdot 2\text{MeOH}$ ) collected using the WorkStation<sup>TM</sup> (Kaiser Optical Systems Inc.) Raman spectrometer.



**Fig. S4.** Overlaid normalized Raman spectra of  $[\text{Ni}_8(\text{O}_2)(\text{abmo})_6(\text{PhCO}_2)_2(\text{MeO})_6(\text{MeOH})_4] \cdot 2\text{MeOH}$  ( $2 \cdot 2\text{MeOH}$ ) and  $[\text{Ni}_8(^{18}\text{O}_2)(\text{abmo})_6(\text{PhCO}_2)_2(\text{MeO})_6(\text{MeOH})_4] \cdot 2\text{MeOH}$  ( $2\text{A} \cdot 2\text{MeOH}$ ) collected using the RamanStation spectrometer (AVALON Instruments).