A Combined Pulsed Electron Paramagnetic Resonance Spectroscopic and DFT Analysis of the $^{13}CO_2$ and ^{13}CO Adsorption in the Metal-Organic Framework $Cu_{2.97}Zn_{0.03}(btc)_2$

- Supporting Information -

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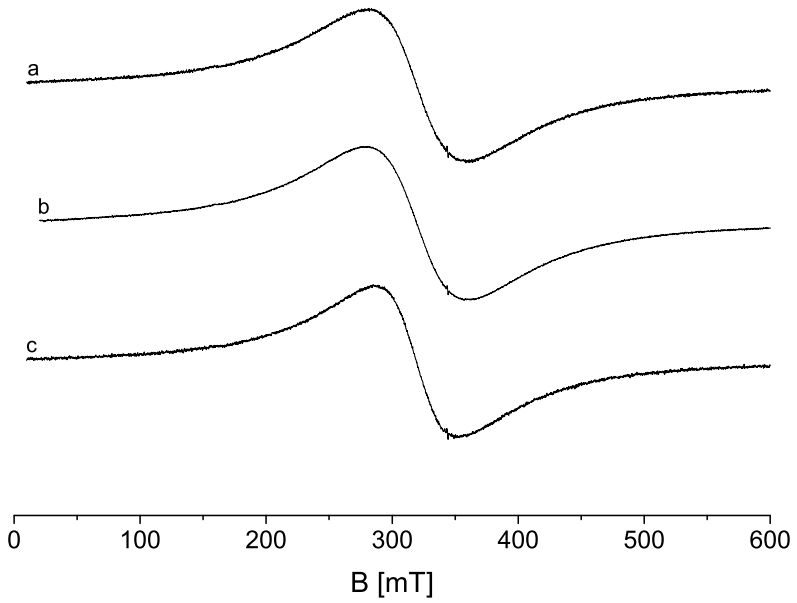


Figure 1: cw EPR spectra at 295 K of a) activated $[Cu_{2.97}Zn_{0.03}(btc)_2]_n$ (**1**), and b) after adsorption of $^{13}CO_2$ (**2**) and c) ^{13}CO (**3**). (ν_{mw} = 9.75 GHz).

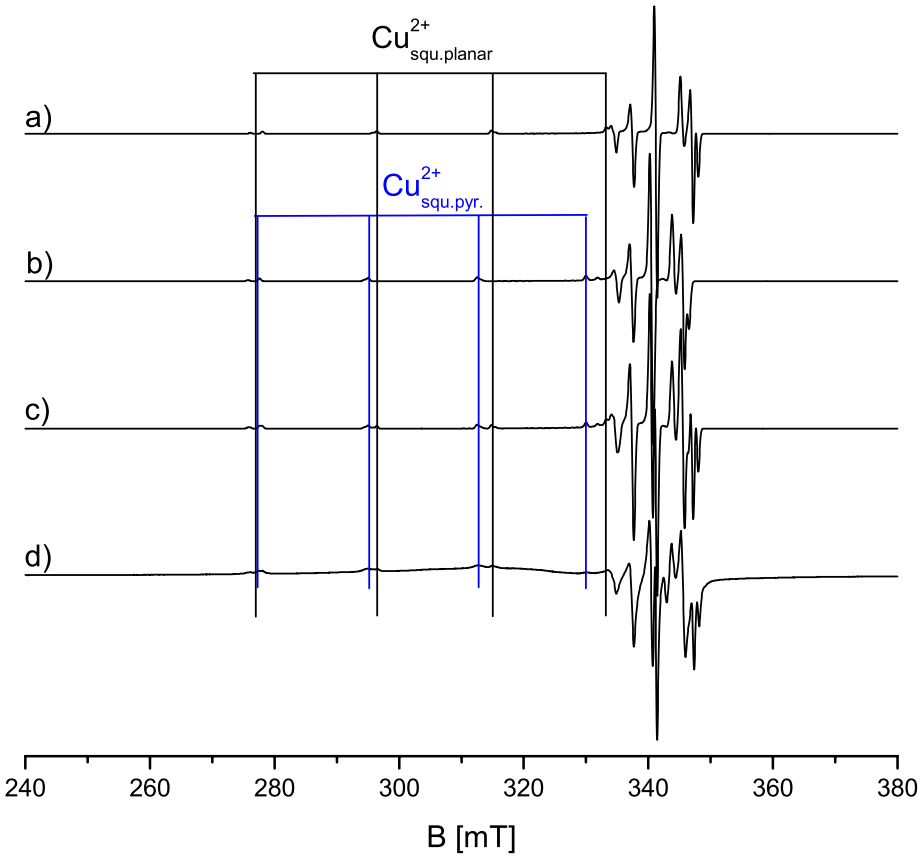


Figure 2: cw EPR spectra at 7 K of $[Cu_{2.97}Zn_{0.03}(btc)_2]_n$ after adsorption of $^{13}CO_2$ (**2**). Spectral simulation of two Cu^{2+} centers: a) with parameters for square planar Cu^{2+} as found in activated **1** and b) with parameters of square pyramidal Cu^{2+} species, c) sum a) + b), and d) experimental spectrum (ν_{mw} = 9.75 GHz). Solid lines indicate the different g_{zz} and A_{zz} values of square-planar (black) and square-pyramidal (blue) Cu^{2+} centers.

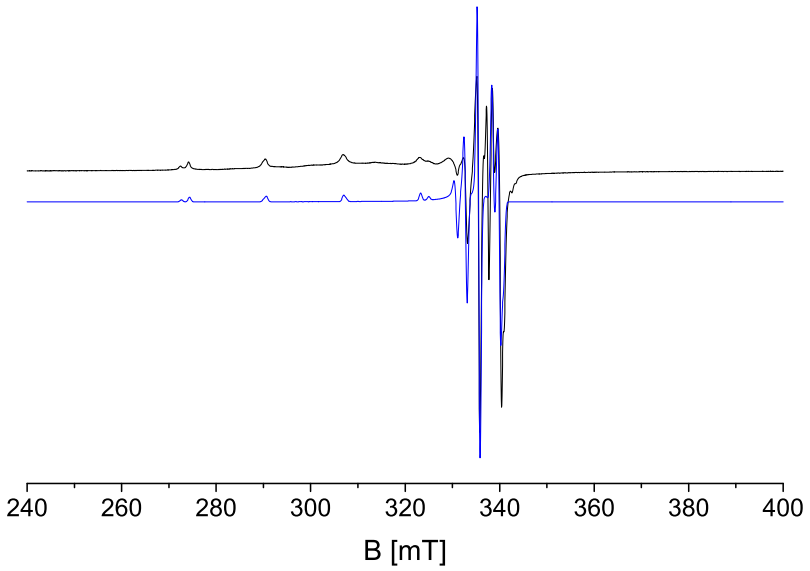


Figure 3: Experimental (a) and simulated (b) cw EPR spectra at 7 K of $[Cu_{2.97}Zn_{0.03}(btc)_2]_n$ after adsorption of ^{13}CO (**3**). (ν_{mw} = 9.75 GHz).

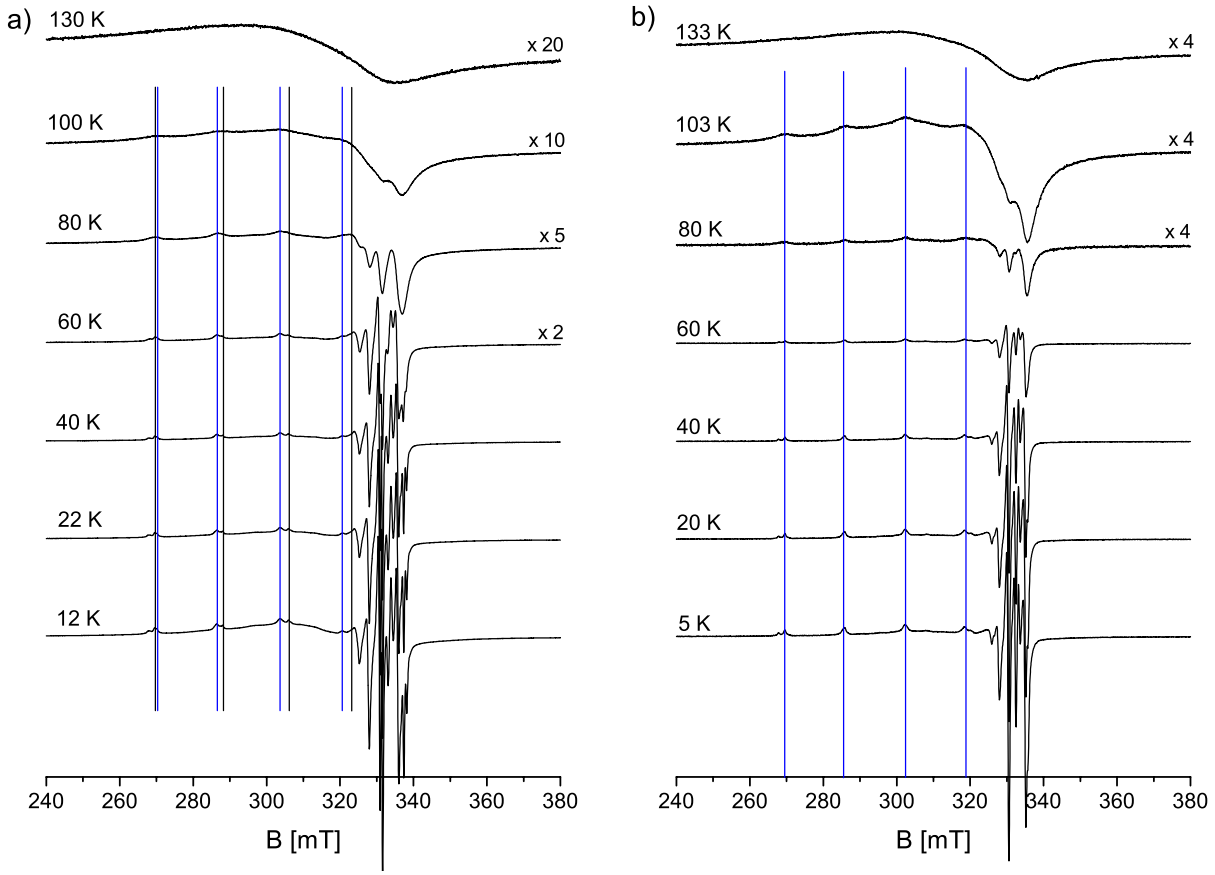


Figure 4: Temperature dependent cw EPR spectra at 7 K of $[Cu_{2.97}Zn_{0.03}(btc)_2]_n$ after adsorption of $^{13}CO_2$ (**2**, left) and ^{13}CO (**3**, right). Spectra at higher temperatures were measured but not shown. Solid lines indicate g_{zz} and A_{zz} parameters of square-pyramidal Cu^{2+} centers with axial ligand (ν_{mw} = 9.47 GHz).

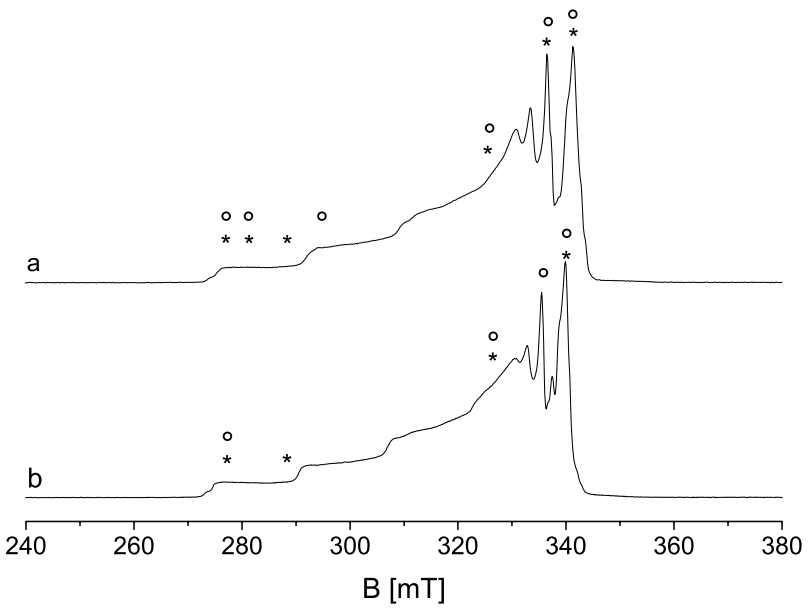


Figure 5: 2p FS ESE spectra at 7 K of $[Cu_{2.97}Zn_{0.03}(btc)_2]_n$ after adsorption of a) $^{13}CO_2$ (**2**) and b) ^{13}CO (**3**). The field positions for HYSCORE experiments are marked with asterisks (*), for pulsed ENDOR experiments with circles (○) (ν_{mw} = 9.75 GHz).

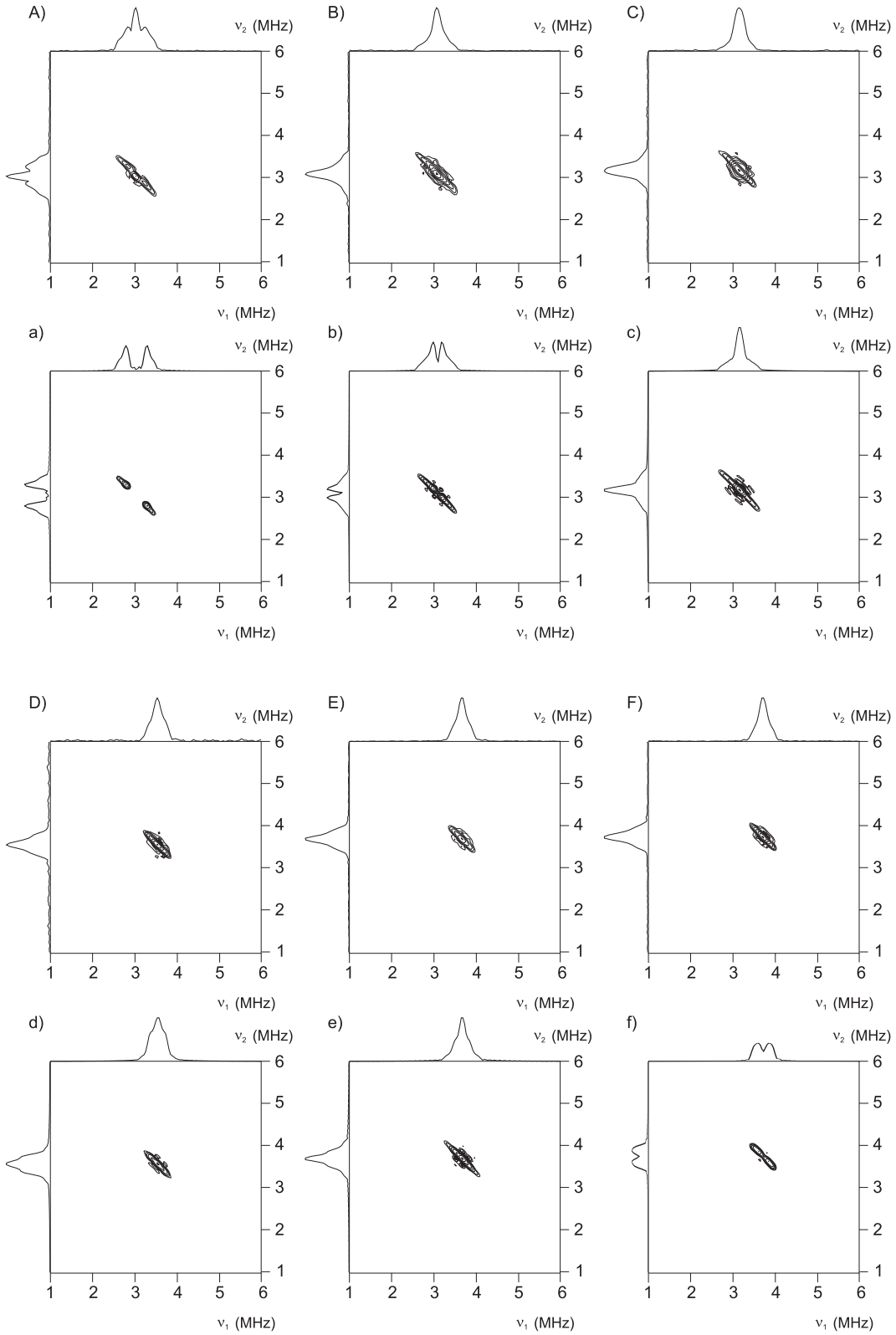


Figure 6: Experimental (A-F) and simulated (a-f) HYSCORE spectra at 7 K of $[Cu_{2.97}Zn_{0.03}(btc)_2]_n$ after adsorption of $^{13}CO_2$ (**2**) at 280.0 mT (A, a), 284.5 mT (B, b), 291.5 mT (C, c), 327.5 mT (D, d), 339.8 mT (E, e) and 344.5 mT (F, f) (ν_{mw} = 9.75 GHz).

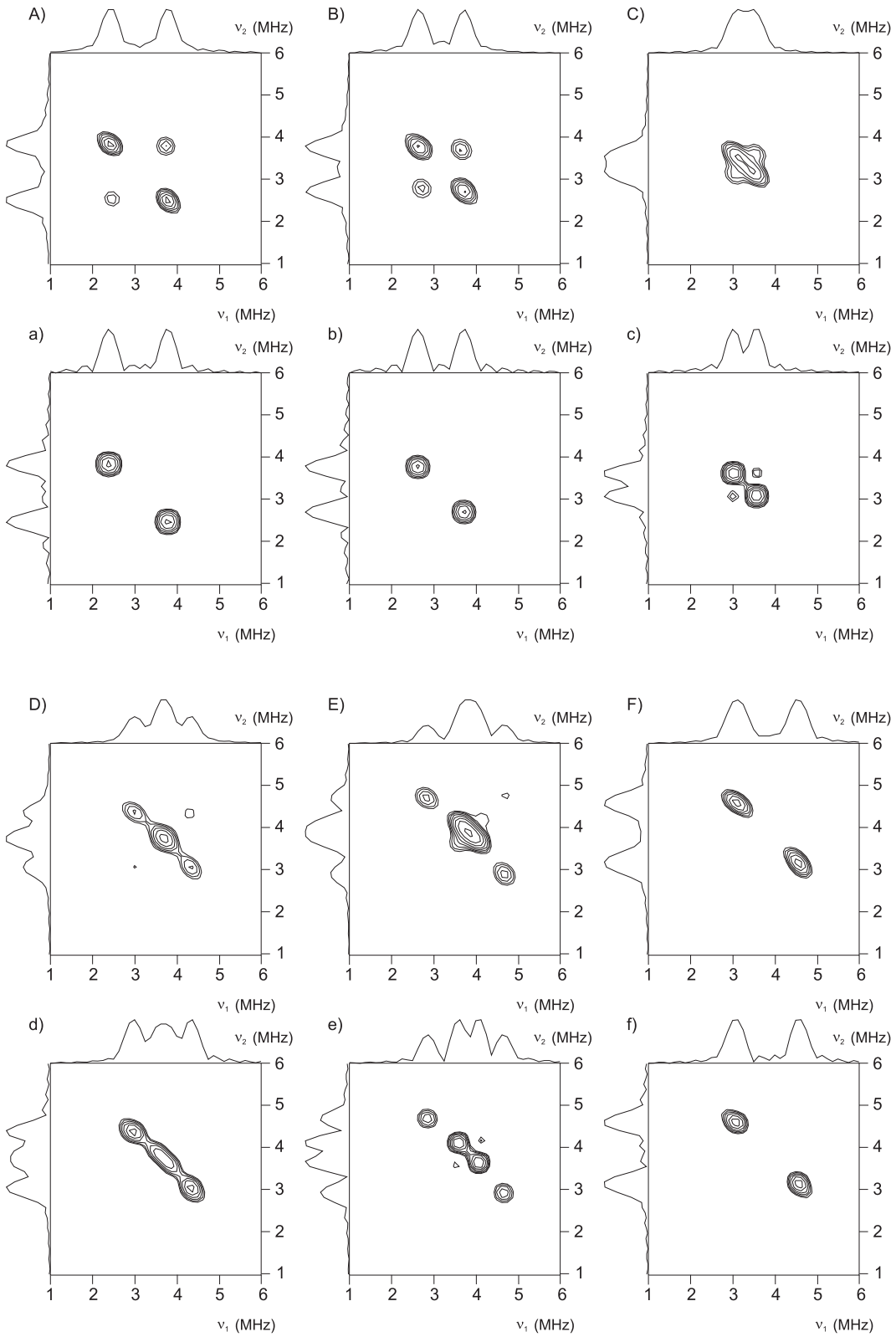
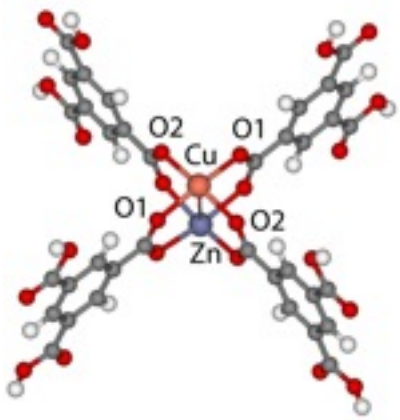


Figure 7: Experimental (A-F) and simulated (a-f) HYSCORE spectra at 7 K of $[Cu_{2.97}Zn_{0.03}(btc)_2]_n$ after adsorption of $^{13}CO_2$ (**2**) at 280.0 mT (A, a), 284.5 mT (B, b), 291.5 mT (C, c), 327.5 mT (D, d), 340.2 mT (E, e) and 344.3 mT (F, f) (ν_{mw} = 9.75 GHz).

Table 1: Calculated interatomic distances and angles of the Cu/Zn paddle wheel units and the O-atoms of the btc ligands in activated $[Cu_{2.97}Zn_{0.03}(btc)_2]_n$ (**1**) and after adsorption of CO_2 (**2**) and CO (**3**), respectively, compared to the parent copper compound $[Cu_3(btc)_2(H_2O)_3]_n$ with coordinated H_2O molecules[a] (**4**) For notation of the atoms, see figure below.

	Distances [angstrom]			Angles [°]			
	Cu-O1/Cu-O2	Zn-O1/Zn-O2	Cu-Zn /Cu-Cu	O1-Cu-O1	O1-Cu-O2	O1-Zn-O1	O1-Zn-O2
1	1.98/1.98	2.05/2.05	2.68	172	90	164	88
2	1.94/2.08	2.10/2.00	2.76	175/141	90	146/170	90
3	1.99/1.99	1.97/1.97	2.56	168	89	174	90
4[a]	1.952(3)/1.952(3)	-/-	2.628(2)	168.2	89.7/89.1	-	-

[a] Distances and angles taken from ref. 1



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