

Formation of Mixed Metal $\text{Cu}_{3-x}\text{Zn}_x(\text{btc})_2$ Frameworks with
Different Zinc Contents: Incorporation of Zn^{2+} into the MOF
Structure as Studied by Solid-State NMR

**Farhana Gul-E-Noor^a, Bettina Jee^a, Matthias Mendt^a, Dieter Hims^b, Andreas Pöpl^a, Martin
Hartmann^b, Jürgen Haase^a, Harald Krautscheid^c, Marko Bertmer^{a*}**

^aInstitute of Experimental Physics II, University of Leipzig, Linnéstr. 5, D-04103 Leipzig, Germany

*^bErlangen Catalysis Resource Centre (ECRC), Friedrich-Alexander-Universität Erlangen-
Nürnberg, Egerlandstr. 3, D-91058 Erlangen, Germany*

*^cFaculty of Chemistry and Mineralogy, University of Leipzig, Johannisallee 29, D-04103 Leipzig,
Germany*

** corresponding author, phone: +49 341 9732617*

FAX: +49 341 9732649

E-mail: bertmer@physik.uni-leipzig.de

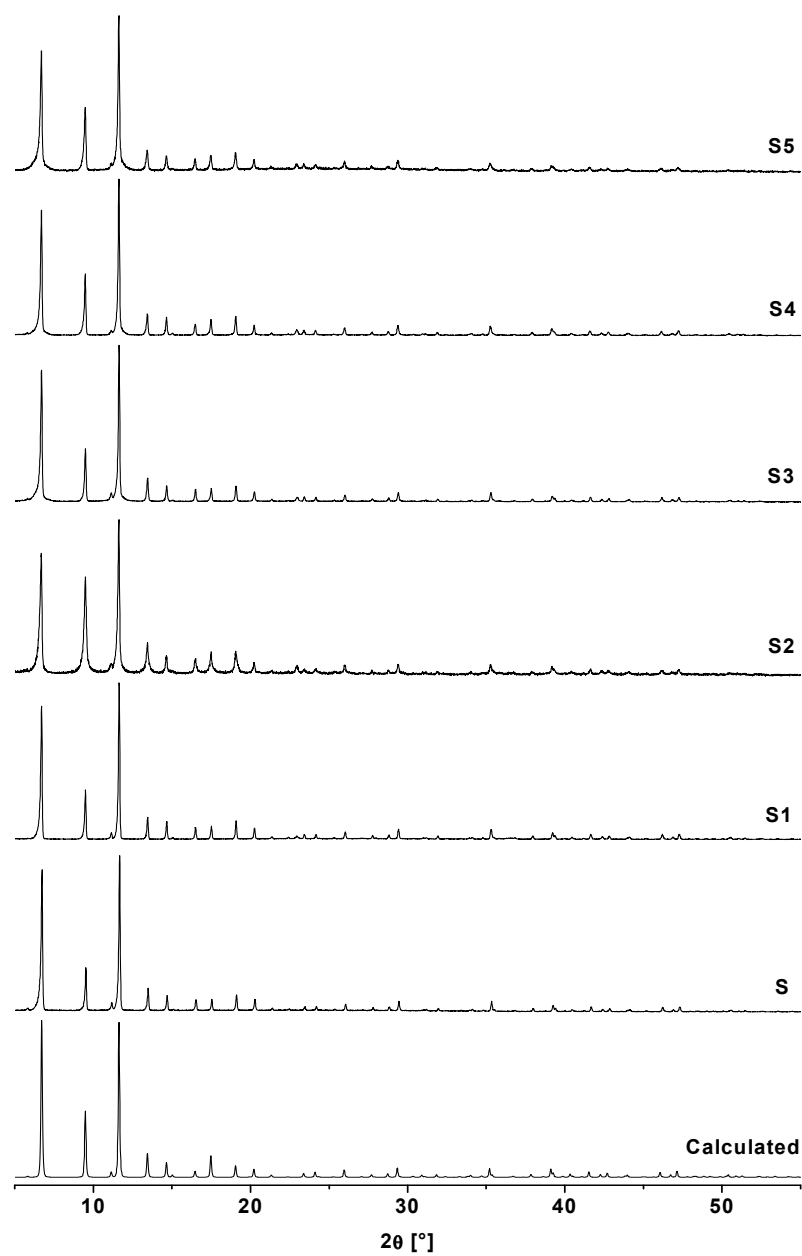


Figure S1: XRD powder patterns of dehydrated $\text{Cu}_3(\text{btc})_2$ (S) and $\text{Cu}_{3-x}\text{Zn}_x(\text{btc})_2$ (S1-S5) samples recorded at 293 K together with the calculated powder pattern based on the single crystal X-ray data of $\text{Cu}_3(\text{btc})_2$ (bottom).

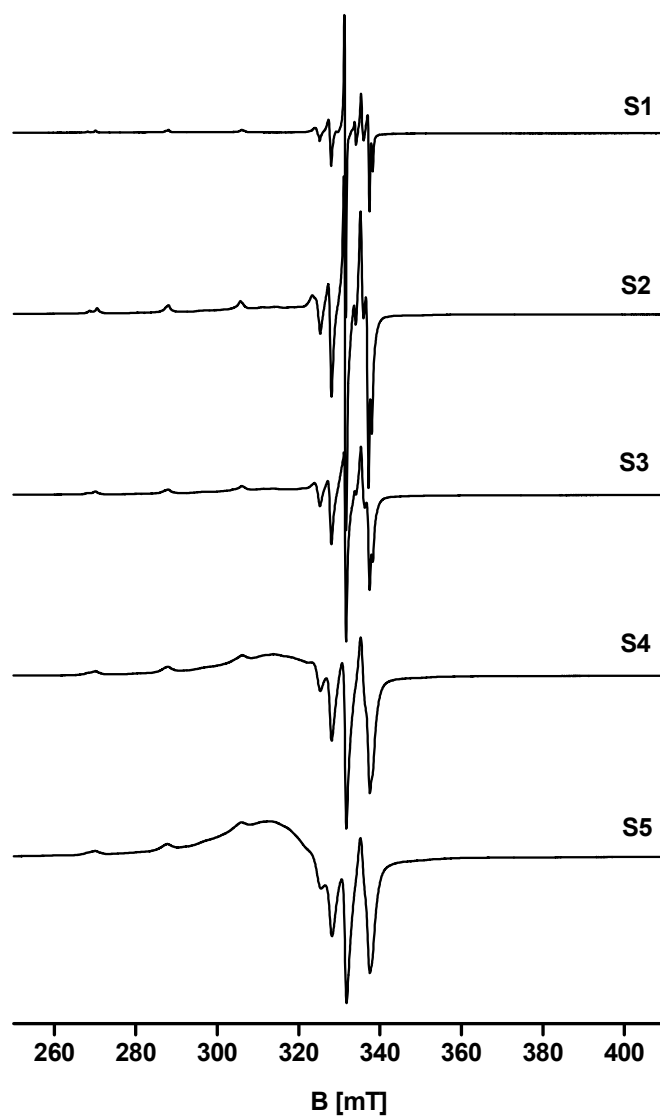


Figure S2: Cw X-band EPR spectra at $T = 7$ K of $\text{Cu}_{3-x}\text{Zn}_x(\text{btc})_2$ (S1-S5).

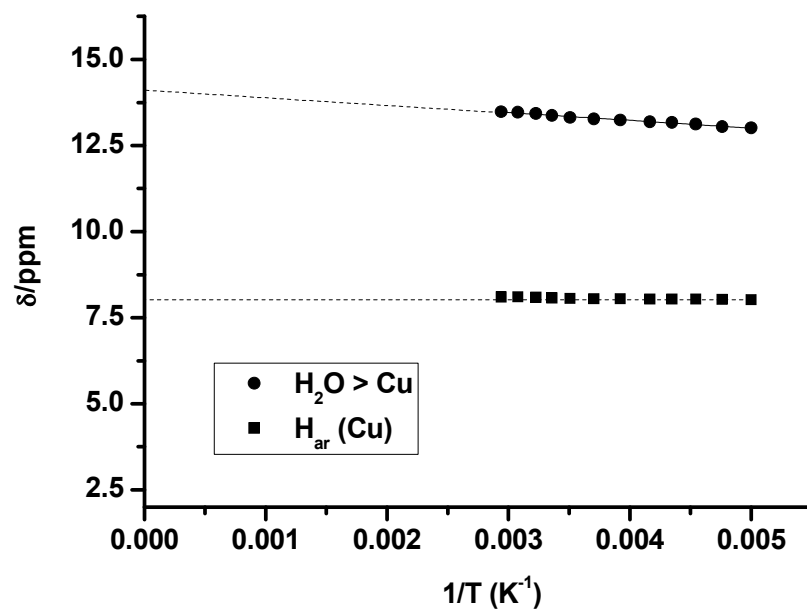


Figure S3: Temperature dependence of the ^1H NMR signals of $\text{Cu}_3(\text{btc})_2$ (with water coordinated to the copper site) in the temperature range from 200 to 340 K.

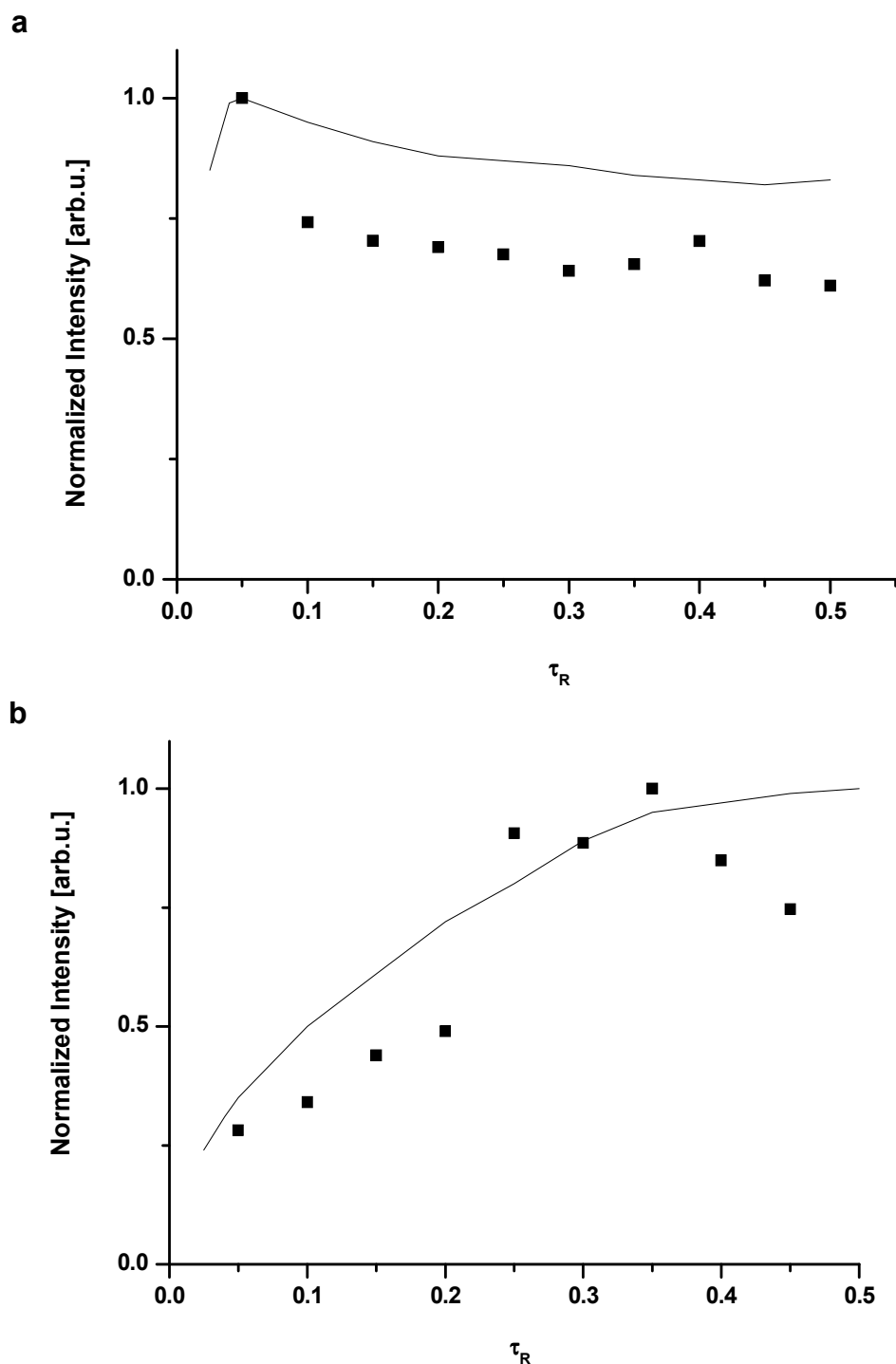


Figure S4: Dipolar INEPT experiment showing the τ -dependence of signal intensity for (a) the 228 ppm signal (^{13}CH) and (b) the -86 ppm signal (^{13}Cq) at a spinning speed of 10 kHz ($\tau_R = 100 \mu\text{s}$). The solid line shows the behaviour of the τ -dependence as adapted from ref. S1 on a sample of $\text{Cu}(\text{DL-alanine})_2$. These data, however, were obtained at a spinning speed of 23.81 kHz. The qualitative agreement let us assign the two signals.

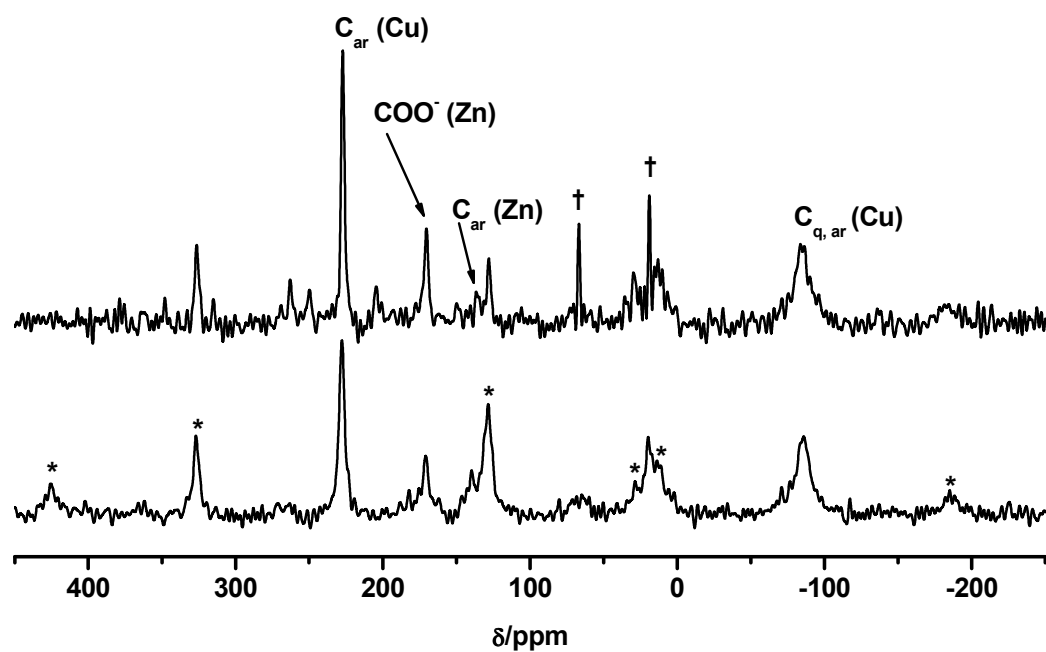


Figure S5: ^{13}C MAS spectra of sample S5 with (top) and without (bottom) high power proton decoupling. Asterisks (shown only in the lower spectrum) denote spinning sidebands. † denote residual solvent signals (ethanol).

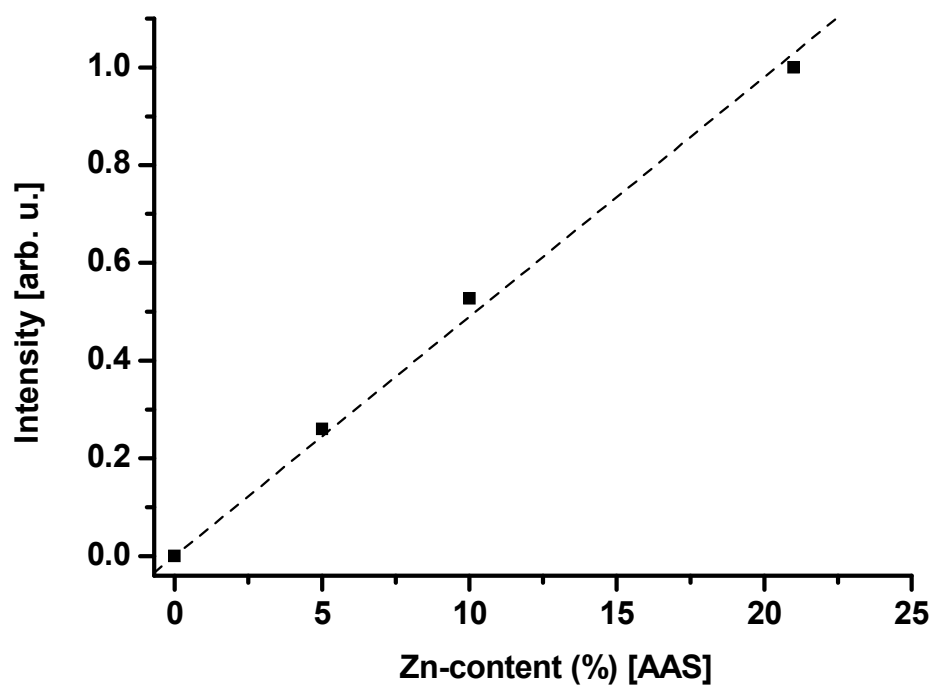


Figure S6: Intensity of the 170.6 ppm signal for $\text{Cu}_3(\text{btc})_2$ (S) and $\text{Cu}_{3-x}\text{Zn}_x(\text{btc})_2$ (S3-S5) vs. zinc content as determined from AAS. For samples S1 and S2 the signal intensity is within the noise level and therefore not included in the plot.

Some details on the pseudocontact shift calculation:

A point-dipole approximation for the magnetic dipole-dipole interaction matrix T between a ^1H and a single electron with a thermally-averaged magnetic moment is considered.

In our case, we have to include both the coupling matrix for the Cu-Cu and Cu-Zn paddle wheels as well as the relative amounts of the electronic $S = 0$ or $S = 1$ state of the Cu-Cu species for a given temperature. For the linear approximation of the thermally-averaged electron magnetic moment $\bar{\mu}_e = A \cdot H_0$ due to the magnetic field H_0 the corresponding matrices A (susceptibilities) in their g-tensor frames are given as follows:^{S2}

Cu-Zn paddle-wheel:
$$A = \frac{\beta^2}{4\kappa T} \begin{bmatrix} g_x^2 & 0 & 0 \\ 0 & g_y^2 & 0 \\ 0 & 0 & g_z^2 \end{bmatrix} \quad (1)$$

(thermally-averaged $S=1/2$ state)

Cu-Cu paddle-wheel:
$$A = \frac{2\beta^2}{3\kappa T} \begin{bmatrix} g_x^2 & 0 & 0 \\ 0 & g_y^2 & 0 \\ 0 & 0 & g_z^2 \end{bmatrix} \quad (2)$$

(thermally-averaged $S=1$ state)

In the case of Cu-Cu pairs the energy splitting between the singlet ground and triplet excited state is obtained from EPR measurements to be $J = -370 \text{ cm}^{-1}$.^{S3} We cannot exclude a thermal averaging of the electron magnetic moment of Cu-Cu pairs due to both the singlet and triplet state. However, this only affects the inhomogeneous line broadening and not the mean values of the calculated pseudocontact shift tensor in comparison to our assumption of thermally populated non-averaged

singlet and triplet states. In our case the calculated inhomogeneous line broadening is too small to decide which thermal averaging of the magnetic Cu-Cu center is valid from the view of the proton.

With the mentioned linear approximation of the thermally-averaged electron magnetic moments, the dipole-dipole Hamiltonian between one electronic magnetic center and the proton takes the typical chemical shift form

$$\hat{H}_{pc} = H_0^T * A^T * T * \hat{\mu}_n, \quad (3)$$

where $\hat{\mu}_n$ is the magnetic moment of the proton.

A program code in Matlab® (2007a, The MathWorks, Natick, Massachusetts, USA) was written, that sums up the Hamiltonians (3) of all electronic paramagnetic centers in the range of a chosen cutoff radius, after transforming these matrices into the crystal frame. It takes a statistical distribution of Cu-Cu and Cu-Zn paddle wheels into consideration, which is consistent with the experimentally determined relative zinc content. Zn-Zn paddle wheels were excluded as they are improbable, as mentioned in this work. For calculating the values in table S1 we chose a cutoff radius of 16 nm and an ensemble size of 12000 possible statistical distributions, which of the 22500 paddle wheels within this radius is Cu-Cu and which is Cu-Zn (or Zn-Cu). Further calculations show, that both, radius and ensemble size, are enough for the convergence of the calculated pseudocontact values within the errors given in table S1.

Table-S1: Calculated pseudocontact (dipolar) shift from only a single and all unpaired electron. For the calculation with all unpaired electrons, the principal tensor components are given as well.

Temperature (K)	δ^{dip} (ppm) (one electron)	all unpaired electrons included			
		S2		S5	
		(P_{xx}, P_{yy}, P_{zz}) ppm	δ^{dip} (ppm)	(P_{xx}, P_{yy}, P_{zz}) ppm	δ^{dip} (ppm)
295	2.13 ± 0.03	(-18.30, -9.64, 33.18)	1.75 ± 0.02	(-17.41, -10.31, 33.04)	1.77 ± 0.02
253	2.48 ± 0.04	(-20.92, -11.57, 38.84)	2.12 ± 0.02	(-20.02, -12.27, 38.63)	2.12 ± 0.02
193	3.25 ± 0.05	(-26.19, -16.17, 51.23)	2.96 ± 0.02	(-25.46, -16.73, 50.86)	2.89 ± 0.02

References:

[S1] Wickramasinghe, N. P.; Ishii, Y. *J. Magn. Reson.* **2006**, 181, 233-243.

[S2] Bloembergen, N. *Physica* **1950**, 16, 95-112.

[S3] Pöpl, A.; Kunz, S.; Himsl, D.; Hartmann, M. *J. Phys. Chem. C* **2008**, 112, 2678-2684.