Supplementary Information

for

Synthesis of copper hydride (CuH) from CuCO₃·Cu(OH)₂ - a path to electrically conductive thin films of Cu

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S.I.1. NMR of paramagnetic compounds

The underlying theory of the NMR analysis of paramagnetic compounds is at present well established.¹⁻⁵ Paramagnetic compounds are known to produce both an additional shift and linewidth broadening of the NMR signal. The shift caused by paramagnetic species—hyperfine shift—is composed of two terms: the Fermi contact and the pseudocontact shift. The Fermi contact shift is transmitted via chemical bonds and has its origins in the scalar coupling between the spin of unpaired electrons and the nuclear spins. The pseudocontact shift is caused by the interaction between the nuclear spins and the magnetic dipole originating from the spins of unpaired electrons.^{4, 5}

The observation of hyperfine shift of copper (II) complex was previously reported by several authors.⁶⁻¹³ Thus, in order to explore the hyperfine shift of Cu (II), we carried out the *in situ* liquid NMR measurements while the reaction was evolving. Synthesis B was investigated and carried out in D₂O instead of H₂O. After the removal of CO₂ and the formation of the Cu(H₂PO₂)₂ complex ($T\approx 273$ K), 500 µL of the reaction mixture were transferred to a 5 mm NMR tube and placed in the NMR spectrometer. The temperature was rapidly raised to 318 K and the reaction was followed by acquisition of the NMR signal as a function of time (approximately one spectrum per minute). Attempts to measure the ³¹P signal from the Cu complex were carried out, but no signal was observed (only a broad peak $v_{1/2}\approx 4000$ Hz was recovered after several hours of the reaction time). This observation is related with the slow electron spin relaxation in Cu (II), which leads to a line broadening effect and consequently loss of the NMR signal of the nuclei close to Cu.^{14, 15}According to the structure of the complex,¹⁶ the P atoms are two bonds way from Cu (II). Thus, Cu (II) is close enough to the P atoms in order to dampen the ³¹P NMR signal.

As opposed to the ³¹P signal, it was possible to detect the ¹H NMR signal. In the beginning of the reaction (*t*=0) two ¹H NMR peaks were observed in the NMR spectrum; a broad peak ($v_{1/2}$ =1974 Hz) at 25.5 ppm, and the water peak ($v_{1/2}$ =77 HZ) at 4.55 ppm (Figure 5 a). As the reaction proceeds, the chemical shift of the observed peaks moves up field (Figure 5 b) and in the last part of the reaction, broad multiplet peaks are observed (Figure 5 c). After two hours of reaction time, only three peaks are visible (Figure 5 d). All the chemical shifts are reported as function of the water peak, which was calibrated to 4.55 ppm, *T*=318 K, according to reported work¹⁷.

Due to the complexity of the reaction and the paramagnetic effect of copper, the unequivocal assignment of the peaks in the NMR spectra is not straightforward. The thermal decomposition of $Cu(H_2PO_2)_2$ in the solid state was previously followed by ¹H NMR. A very broad signal around 200 ppm (recorded at *T*=153 K), which shifts to close to 0 ppm after the total thermal decomposition, was observed.¹⁸ This observation of hyperfine shift qualitatively agrees with our ¹H NMR measurements. However, the hyperfine shift of the broad peak that we observe is one order of magnitude lower (δ ~ 26 ppm) and the linewidth is also narrower. The observed difference in the hyperfine shifts may be to 1) the high difference in temperatures at which the spectra were recorded (*T*=153 vs *T*=318K) and 2) the physical state of the sample (solid vs liquid)—which in a isotropic liquid the rapidly tumbling of the molecules will average the chemical shift anisotropy resulting in a isotropic chemical shift and narrower lines.^{19, 20} Moreover, the hyperfine shifts is also dependent in the number of electron per volume (*N*). ²¹ Therefore, since *N* is higher in the solid, larger hyperfine shifts are observed.

As concerning the solvation of the copper (II) complex, the average residence time (τ_{H2O}) of water molecules in the first coordination shell for Cu²⁺ is in the order of 10⁻⁹ s.²²⁻²⁴ Thus, if some water molecules are coordinated with the copper, the contribution to the NMR signal will be minimum, since the average chemical shift will be dominated by the signal of the free solvent. This fact also supports that the broad peak ($\delta = 26$ ppm) observed in the beginning of the reaction corresponds to the complex Cu(H₂PO₂)₂.



S.I.2. Time evolution of ¹H NMR spectra of the reaction liquid media

S.I. Figure 1. ¹H NMR spectra of the reaction liquid media, at *T*=318K, at different reaction times. Contrary to the broad peak at higher chemical shifts, the peaks at δ =6.5 ppm and δ =7.2 ppm (labeled with *) do not change during the course of the reaction. The data is offset in y axis for easier visualization.

S.I.3. Calibration curve based in the hyperfine shift vs. copper (II) concentration

The calibration curve was carried out by preparing 5 standard samples with different concentrations of CuCO₃·Cu(OH)₂ (Note that the H₃PO₂ concentration was always kept constant). After the CuCO₃·Cu(OH)₂ dissolution by CO₂ removal ($T \approx 273$ K), the standard samples were transferred to the NMR tube and the ¹H NMR signal was recorded (Figure 2a –S.I.).



S.I. Figure 2. ¹H-NMR spectra of the reaction media with different [Cu²⁺], *T*=274.2 K (a); calibration curve relative chemical shift $(\delta/\Delta\delta_i)$ as function of [Cu²⁺].

In order to minimize any possible Cu²⁺ consumption, the ¹H NMR measurements of the calibration samples were carried out at *T*=274 K. However, since the hyperfine chemical shift is temperature dependent^{2, 4, 5}, instead of reporting the absolute chemical shift δ , we report the relative chemical shift (δ/δ_i) , where δ_i is the chemical shift of the sample with higher [Cu²⁺] (0.266 M), and δ is the observed chemical shift of the samples with lower [Cu²⁺]. Consequently, this approach minimizes the discrepancies between the chemical shift of the calibration curve (*T*= 274 K) and the measurements of the studied reaction at *T*=318 K. A hyperbolic function was fitted to the δ/δ_i as function of [Cu²⁺] (Figure 2 b –S.I.).

Based in the obtained calibration curve, the $[Cu^{2+}]$ during the course of reaction was estimated by converting the relative chemical shift (δ/δ_i) of the Cu(H₂PO₂)₂ peak, where δ_i corresponds to the hyperfine shift at *t*=0. In the last part of the reaction, when duplets and triplets are present, the hyperfine shift δ reported corresponds to the central part of the peaks.

References

- 1. I. Bertini, C. Luchinat and P. Giacomo, in *Current Methods in Inorganic Chemistry*, Elsevier, 2001.
- 2. I. Bertini, C. Luchinat and G. Parigi, *Progress in Nuclear Magnetic Resonance Spectroscopy*, 2002, **40**, 249-273.
- 3. M. Kaupp and F. H. Köhler, *Coordination Chemistry Reviews*, 2009, **253**, 2376-2386.
- 4. G. N. La Mar, W. D. Horrocks and R. H. Holm, *NMR of Paramagnetic Molecules: Principles and Applications*, Academic Press, New York, 1973.
- 5. M. Enders, in *Modeling of Molecular Properties*, Wiley-VCH Verlag GmbH & Co. KGaA, 2011, DOI: 10.1002/9783527636402.ch4.
- 6. H. Sternlicht, R. G. Shulman and E. W. Anderson, *The Journal of Chemical Physics*, 1965, **43**, 3123.
- 7. W. G. Espersen, W. C. Hutton, S. T. Chow and R. B. Martin, *Journal of the American Chemical Society*, 1974, **96**, 8111-8112.
- 8. A. Boyer and G. V. Fazakerley, *Journal of Inorganic and Nuclear Chemistry*, 1981, **43**, 1955-1961.
- 9. B. Henry, J.-C. Boubel and J.-J. Delpuech, *Polyhedron*, 1985, 4, 1069-1077.
- 10. Z. Árkosi, Z. Paksi, L. Korecz, T. Gajda, B. Henry and A. Rockenbauer, *Journal of Inorganic Biochemistry*, 2004, **98**, 1995-2005.
- 11. A.-S. Felten, N. Pellegrini-Moïse, K. Selmeczi, B. Henry and Y. Chapleur, *European Journal of Organic Chemistry*, 2013, 2013, 5645-5654.
- 12. E. Faggi, R. Gavara, M. Bolte, L. Fajari, L. Julia, L. Rodriguez and I. Alfonso, *Dalton Transactions*, 2015, 44, 12700-12710.
- 13. K. Du and T. D. Harris, *Journal of the American Chemical Society*, 2016, **138**, 7804-7807.
- 14. A. P. Kalverda, J. Salgado, C. Dennison and G. W. Canters, *Biochemistry*, 1996, **35**, 3085-3092.
- 15. I. Bertini, L. Banci and C. Luchinat, in *Methods in Enzymology*, Academic Press, 1989, vol. Volume 177, pp. 246-263.
- 16. D. Y. Naumov, M. I. Naumova, N. V. Kuratieva, E. V. Boldyreva and J. A. K. Howard, *Acta Crystallographica Section C*, 2002, **58**, i55-i60.
- 17. H. E. Gottlieb, V. Kotlyar and A. Nudelman, *The Journal of Organic Chemistry*, 1997, **62**, 7512-7515.
- 18. O. I. Lomovsky, Y. I. Mikhailov, V. V. Boldyrev and V. M. Mastikhin, *Thermochimica Acta*, 1981, **43**, 135-141.
- 19. M. J. Duer, in *Solid-State NMR Spectroscopy Principles and Applications*, Blackwell Science Ltd, 2007, DOI: 10.1002/9780470999394.ch1, pp. 1-72.
- 20. M. Levitt, *Spin dynamics: basics of nuclear magnetic resonance*, John Wiley and Sons, Ltd, Chichester, 2008.
- 21. J. P. Yesinowski, in *Solid State NMR*, ed. J. C. C. Chan, Springer Berlin Heidelberg, Berlin, Heidelberg, 2012, DOI: 10.1007/128_2011_208, pp. 229-312.
- 22. L. Helm and A. E. Merbach, Chemical Reviews, 2005, 105, 1923-1960.
- 23. A. Pasquarello, I. Petri, P. S. Salmon, O. Parisel, R. Car, É. Tóth, D. H. Powell, H. E. Fischer, L. Helm and A. E. Merbach, *Science*, 2001, **291**, 856-859.

24. D. H. Powell, L. Helm and A. E. Merbach, *The Journal of Chemical Physics*, 1991, **95**, 9258-9265.