On Verdigris, Part I: Crystal Structure Solution and Characterization of $Cu_3(CH_3COO)_2(OH)_4$

- Supporting Information -

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ADDITIONAL TABLES AND FIGURES

Table S 1. Crystallographic and Rietveld Refinement data of the 1-2-0 phase at 303 K.

compound name	1-2-0 phase
molecular formula	$Cu_3(CH_3COO)_2(OH)_4$
sum formula	$C_4H_{10}Cu_3O_8$
molecular weight (g/mol)	376.75
space group	*Pbca*(61)
Z	8
a /Å	20.9742(1)
b /Å	7.2076(1)
c /Å	13.1220(1)
α /°	90
β /°	90
γ /°	90
V /Å³	1983.69(2)
ρ_{calc}/ g · cm^{-3}	2.52
Wavelength / Å	0.8260
R-exp /% *	1.11
R-p /% *	8.68
R-*w*p /% *	8.32
R-F^2 /% *	4.12
starting angle (° 2θ)	3.0
final angle (° 2θ)	60.0
step width (° 2θ)	0.001
time/scan (min)	15
no. of variables	78

* *R*-exp, *R*-p, *R*-*w*p, *R*-F^2 and G.O.F. as defined in TOPAS (Bruker AXS)

Table S 2. Atomic coordinates of the 1-2-0 phase at 303 K.

Atom	**Wyck.**	**Site**	**S.O.F.**	***x/a***	***y/b***	***z/c***	**B /Å²**
Cu1	8c	1	1	0.9000(1)	0.374(1)	0.2551(2)	0.83(3)
Cu2	8c	1	1	0.0061(1)	0.295(1)	0.6304(1)	0.83(2)
Cu3	8c	1	1	0.0053(1)	0.196(1)	0.3794(1)	0.83(2)
O1	8c	1	1	0.9622(2)	0.161(1)	0.2493(7)	0.77(7)
O2	8c	1	1	0.9480(2)	0.747(1)	0.9891(6)	0.77(7)
O3	8c	1	1	0.5456(3)	0.930(1)	0.1323(5)	0.77(7)
O4	8c	1	1	0.9756(3)	0.439(1)	0.3747(5)	0.77(7)
C11	8c	1	1	0.1439(5)	0.659(1)	0.0912(5)	2.82(8)
C12	8c	1	1	0.1941(8)	0.532(2)	0.0468(9)	2.82(8)
O11	8c	1	1	0.0899(8)	0.646(3)	0.0511(12)	2.82(8)
O12	8c	1	1	0.1635(13)	0.764(2)	0.1652(9)	2.82(8)
C21	8c	1	1	0.8617(5)	0.750(1)	0.7303(4)	2.82(8)
C22	8c	1	1	0.8143(7)	0.620(2)	0.6856(7)	2.82(8)
O21	8c	1	1	0.8433(11)	0.911(2)	0.7393(10)	2.82(8)
O22	8c	1	1	0.9144(7)	0.694(3)	0.7549(8)	2.82(8)

Table S 3. Selected bond lengths and distances of the 1-2-0 phase at 303 K.

Atoms	**Distance**	**Atoms**	**Distance**	**Atoms**	**Distance**	**Atoms**	**Distance**
Cu1-O1	2.019(4) Å	Cu2-O1	1.839(8) Å	Cu3-O1	1.949(8) Å	C11-O11	1.253(12) Å
Cu1-O3	2.017(7) Å	Cu2-O2	1.872(7) Å	Cu3-O2	2.017(7) Å	C11-O12	1.300(10) Å
Cu1-O12	1.869(22) Å	Cu2-O3	1.950(6) Å	Cu3-O3	2.099(6) Å	C11-C12	1.511(12) Å
Cu1-O21	1.967(17) Å	Cu2-O4	1.957(6) Å	Cu3-O4	1.862(6) Å	C21-O21	1.220(11) Å
Cu1-O4	2.281(7) Å	Cu2-O22	2.362(17) Å	Cu3-O11	2.226(19) Å	C21-O22	1.225(8) Å
				Cu3-O22	2.565(12) Å	C21-C22	1.490(11) Å
Atoms		**Angle**	**Atoms**		**Angle**		
O11-C11-O12		130(1)	O21-C21-O22		125(1)		
O11-C11-C12		115(1)	O21-C21-C22		115(1)		

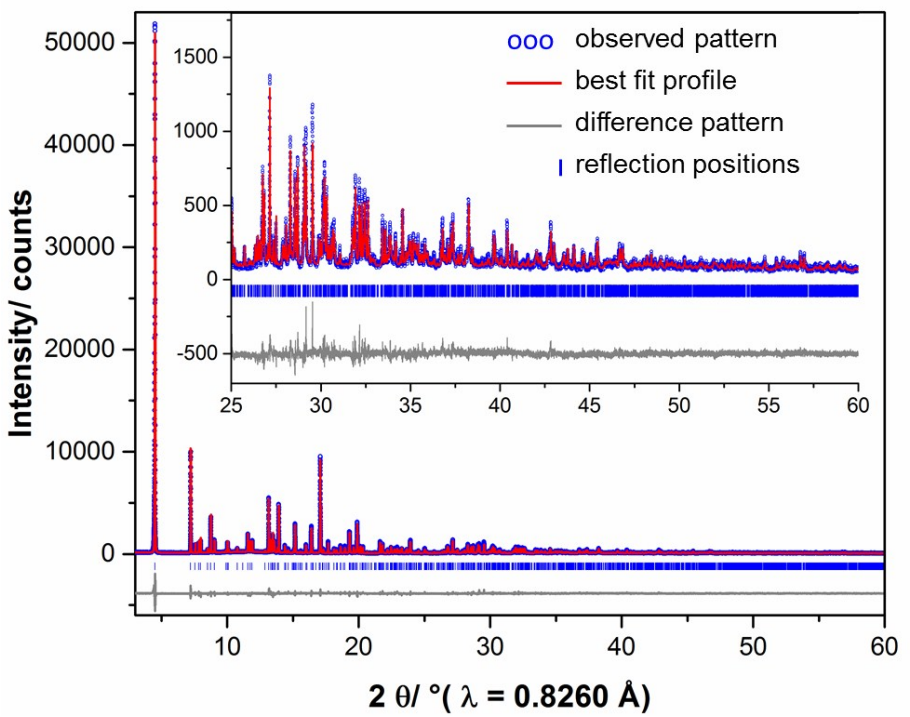

Figure S 1. Scattered X-ray intensities of the 1-2-0 phase at 303 K as a function of diffraction angle 2θ. The observed pattern (circles) measured in Debye-Scherrer geometry, the best Rietveld fit profiles (line) and the difference curve between the observed and the calculated profiles (below) are shown. The high angle part starting at 25.0° in 2θ is enlarged for clarity.

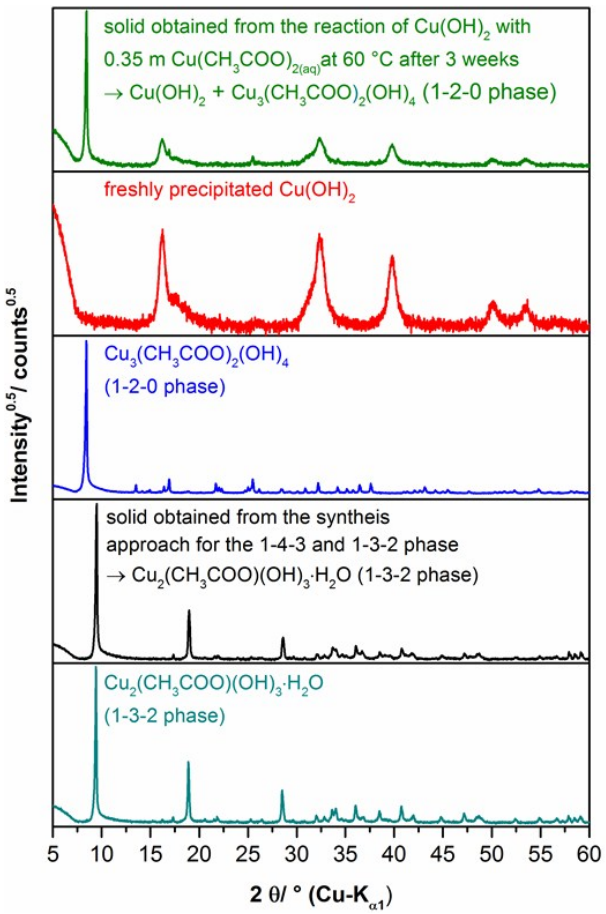

Figure S 2. XRPD patterns of various solid products and intermediates of the synthesis approaches for basic copper acetates.

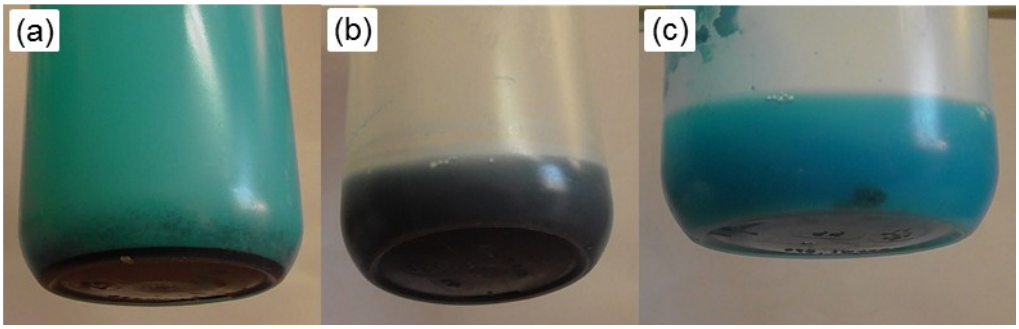

Figure S 3. Photographs of the polypropylene vessels in which freshly precipitated $Cu(OH)_2$ was reacted with copper(II)-acetate solutions for 40 d, (a) rection with 0.05 m $Cu(CH_3COO)_{2(aq)}$, (b) rection with 0.15 m $Cu(CH_3COO)_{2(aq)}$, (c) rection with 0.35 m $Cu(CH_3COO)_{2(aq)}$, the black color indicates the presence of CuO.

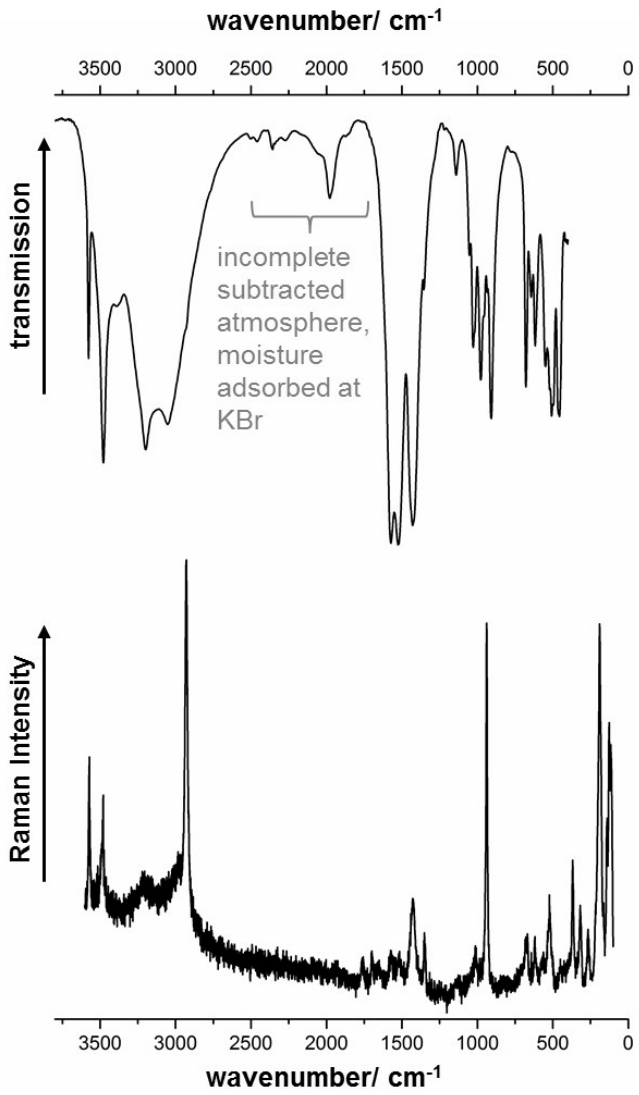

Figure S 4. Complete IR- (top) and Raman- (bottom) spectrum of the 1-2-0 phase.

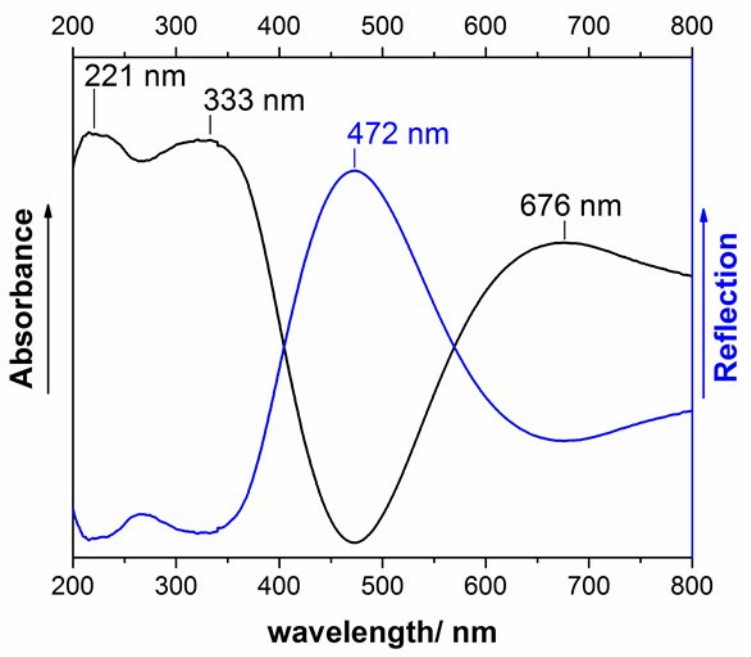

Figure S 5. UV/VIS reflectance spectrum of the 1-2-0 phase.

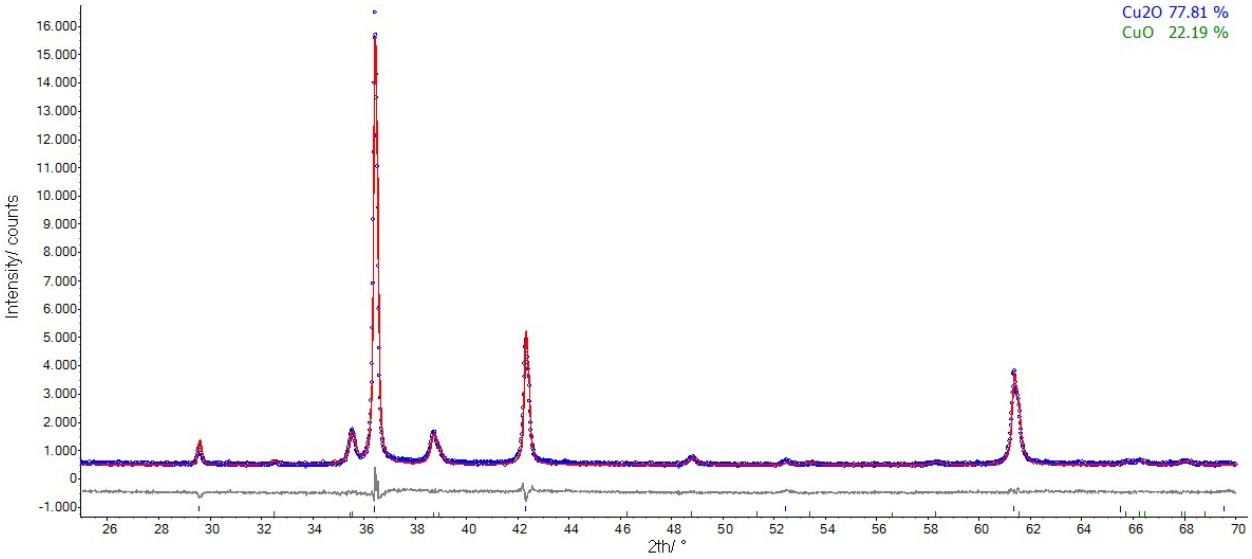

Figure S 6. Quantitative phase analysis of the residue of the thermal decomposition of the 1-2-0 phase after heating the sample up to 450 °C.

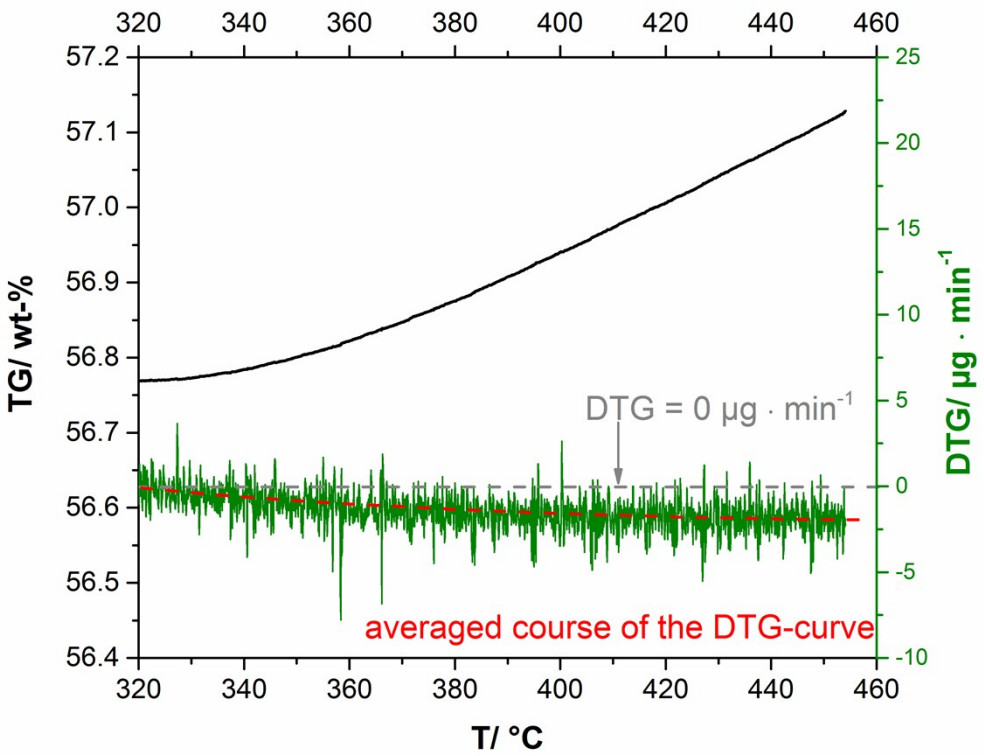

Figure S 7. Excerpt of the thermal analysis in the range between 320 °C and 450 °C, the oxidation of Cu_2O is indicated by the increase of the mass of the residue (TG curve, black line) and by the negative DTG values (green line, red trend line).