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Synthesis, crystal structure and thermal stability of new copper(II) trichloroacetate complexes

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In the paper we report the synthesis and crystal structure of two new complexes based on trichloroacetate copper (II) with the crystallographic formulae $Cu_2(CCl_3COO)_3(OH)(H_2O)_4 \cdot H_2O$ (**1**) and $Cu(CCl_3COO)_2(MeCN)$ (**2**). Here we show supplementary materials to our work.

Instrumental analysis description

Thermal behavior. TA was performed by a NETZSCH STA 409 PC *Luxx*® thermal analyzer (NETZSCH, Germany) in a temperature range from 40 to 800 °C. A heating rate of 5 °C min^{-1} and dynamic argon atmosphere with flow rate of 30 ml min^{-1} were used. The sample weight was at least 10 mg. The composition of the gas phase formed upon decomposition of the samples was studied using a QMS 403C Aëolos quadrupole mass spectrometer (NETZSCH, Germany) coupled to the NETZSCH STA 409 PC Luxx thermal analyzer. Mass spectra (MS) were recorded for several mass numbers (*m/z*) (Table S3 and Figure S1).

ATR spectroscopy. The IR spectra were recorded in the 4000 – 650 cm^{-1} using the spectrometer Nicolet 8700 (Thermo Scientific). The resolution was 4 cm^{-1}, using Blackman-Harris apodization and Mertz phase correction.

Powder X-Ray diffraction (PXRD) study was performed on a Rigaku D/MAX 2500 diffractometer (Cu *Kα* radiation) with a rotating anode (graphite monochromator). The peak profiles were described using a pseudo-Voigt function. The background profiles were described by quartic polynomial. Samples were analyzed using an X-ray amorphous film, and the sample preparation was carried out in nitrogen atmosphere.

CHN analysis was carried out on a Carlo Erba 1106 elemental analyzer (Carlo Erba, Milan, Italy).

Table S1. The comparison between bond lengths (in Å) in the obtained compound **1** with the published data (abbr.: OHip = 5-hydroxyisophthalate, tpht = terephthalate, bpym = 2,2'-bipyrimidine, CNip = 5-cyanoisophthalate).

Compound	Structural type	Ligand			
		$RCOO^-$ basal	H_2O		OH^- basal
			apical	basal	
1, chain fragment	polymer	2.008(4) – 2.025(4)	2.364(4) – 2.428(4)	–	1.925(3) – 1.931(3)
1, molecular fragment	monomer	1.922(4) – 1.949(4)	2.350(4)	1.953(4) – 1.997(4)	–
$Cu(CCl_3COO)_2(H_2O)_3$ [S1]	monomer	1.954(4)	2.183(5)	1.968(4)	–
$Cu(CF_3COO)_2(H_2O)_4$ [S2]	monomer	1.967(5) – 2.003(5)	2.435(6) – 2.459(7)	1.931(5) – 1.943(5)	–
$Cu(CHF_2COO)_2(H_2O)_{0.5}$ [S3]	polymer	1.935(3) – 1.953(2)	2.315(3)	–	–
$Cu(CH_2ClCOO)_2(H_2O)_{1.5}$ [S4]	dimer	1.9553(15) – 1.9783(16)	2.102(2) – 2.142(2)	–	–
$[Cu_3(OHip)_2(OH)_2(H_2O)_4](H_2O)_4$ [S5]	trimer	1.932(3) – 1.983(3)	2.420(3) – 2.455(2)	1.929(2) – 1.978(3)	1.864(2) – 1.964(3)
$\{[Cu_3(tpht)_2(OH)_2(H_2O)_4](bpym)\}_n$ [S6]	polymer	1.9522(15) – 2.0402(14)	2.3891(18) – 2.4302(18)	–	1.9076(15) – 1.9096(15)
$[Cu_3(CNip)_2(OH)_2(H_2O)_2]_n$ [S7]	polymer	1.918(2) – 1.957(2)	2.303(2) – 2.501(3)	–	1.961(2) – 1.999(2)

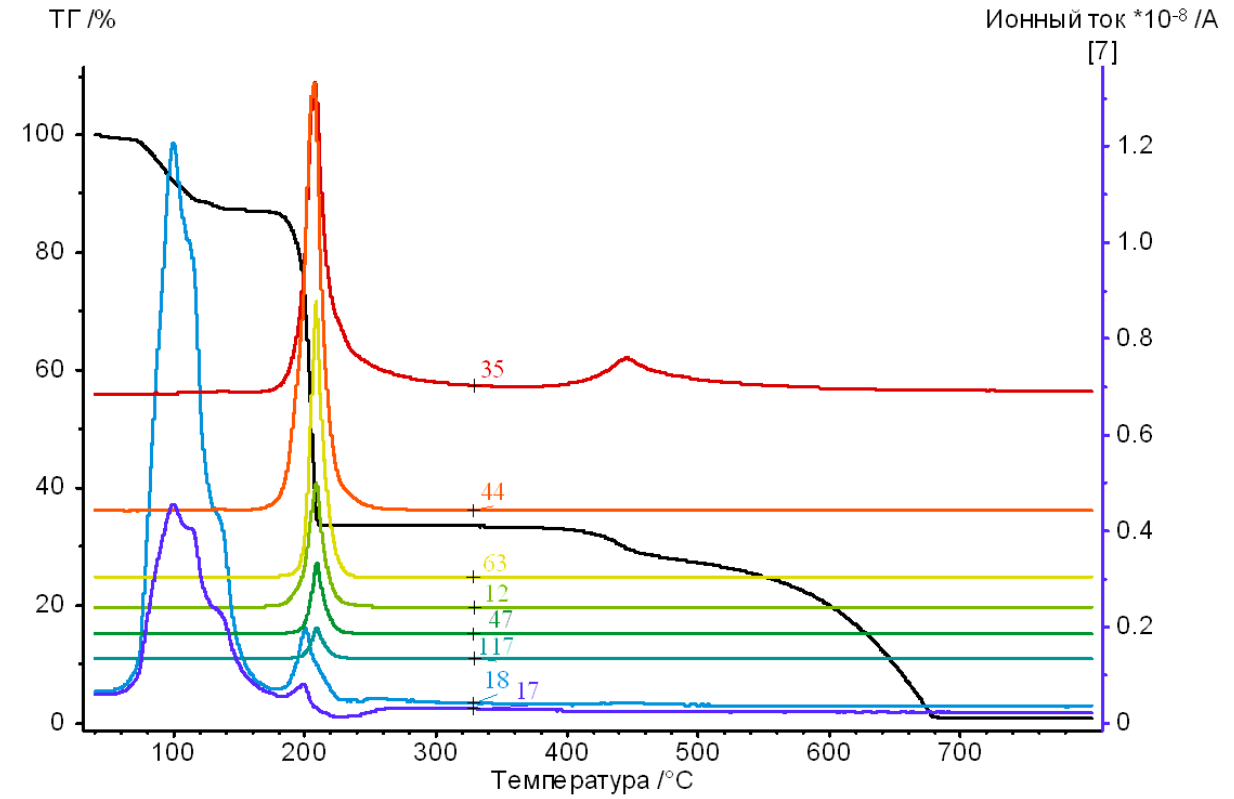
Table S2. The comparison between bond lengths (in Å) in the obtained compound **2** with the published data.

Compound	**Structural type**	**Ligand**	
		$RCOO^-$ basal	**MeCN apical**
2	dimer (paddle wheel)	1.964(3) – 1.973(3)	2.158(4)
$Cu(CH_2FCOO)_2(MeCN)_{1.5}$ [S8]		1.954(3) – 1.977(3)	2.161(4) – 2.177(4)
$Cu(CHCl_2COO)_2(MeCN)$ [S9]		1.938(3) – 2.002(3)	2.140(4) – 2.157(4)
$Cu(CF_3COO)_2(MeCN)$ [S10]		1.964(3) – 1.972(2)	2.114(2)
$Cu(CH_3COO)_2(MeCN)_{1.5}$ [S11]		1.961(3) – 1.968(3)	2.203(4)

Table S3. Mass numbers (*m/z*).

Fragment	Mass number (*m/z*)
C^+	12
N^+ / CH_2^+	14
NH_2^+ / O^+	16
NH_3^+ / OH^+	17
H_2O^+	18
CO^+/ N_2^+	28
Cl^+	35
$MeCN^+$	41
CO_2^+	44
CCl^+	47
$COCl^+$	63
CCl_3^+	117

Figure S1. Mass spectra of gaseous products of decomposition reaction were recorded for several mass numbers (*m/z*) for **1** (top) and **2** (bottom).



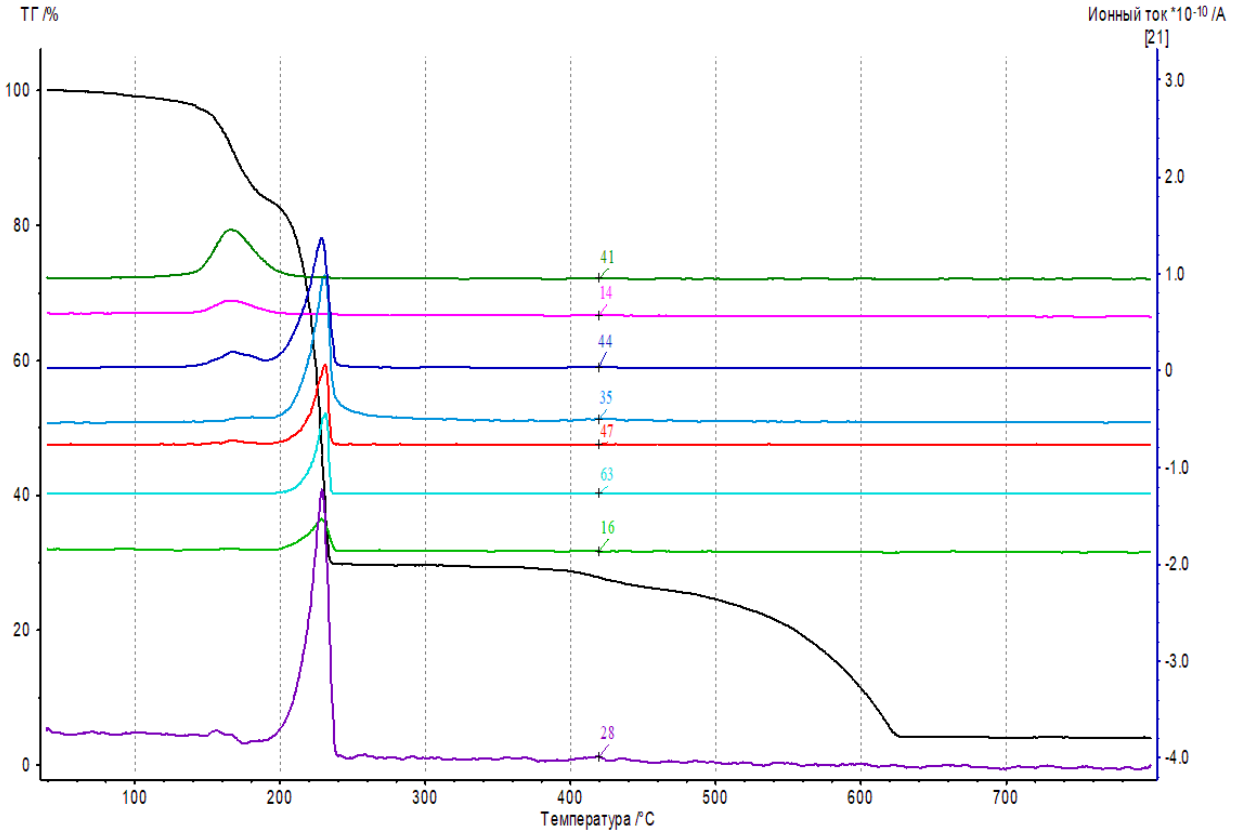


Figure S2. IR spectra for new compounds in comparison with one for a known trihydrate trichloroacetate copper (II).

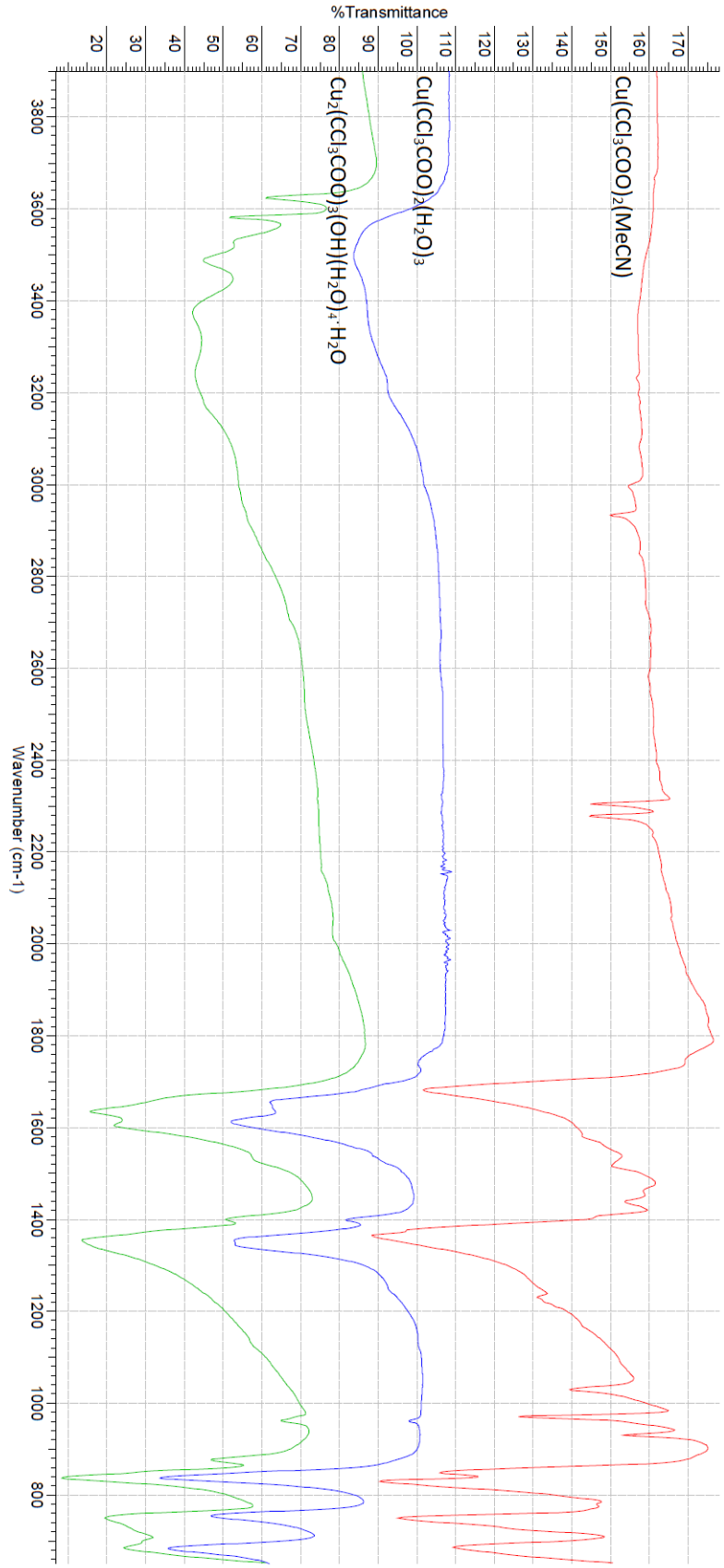


Table S4. IR spectra for new compounds **1** and **2** in comparison with one for a known trihydrate trichloroacetate copper (II), $Cu(CCl_3COO)_2(H_2O)_3$.

$Cu(CCl_3COO)_2(H_2O)_3$	**1**	**2**	**Assignment**
3700 - 2900	3624 3581 3550 - 2700		ν (O-H)
		2995 2933	ν (CH_3)
		2305 2278	ν (C≡N) δ (CCN)
1655 1612	1635 1605	1682	ν_{as} (COO)
		1438	δ (CH_3)
1399 1354	1400 1354	1365	ν_s (COO)
		1030	δ (CH_3)
961	962	970 930	ν_s (C-C)
837 755	875 837 750	849 829 750	ν_{as} (CCl_3)
684	685	687	ν_s (CCl_3) / δ (COO)

Figure S3. PXRD data for **1** (blue) and its theoretical pattern (red).

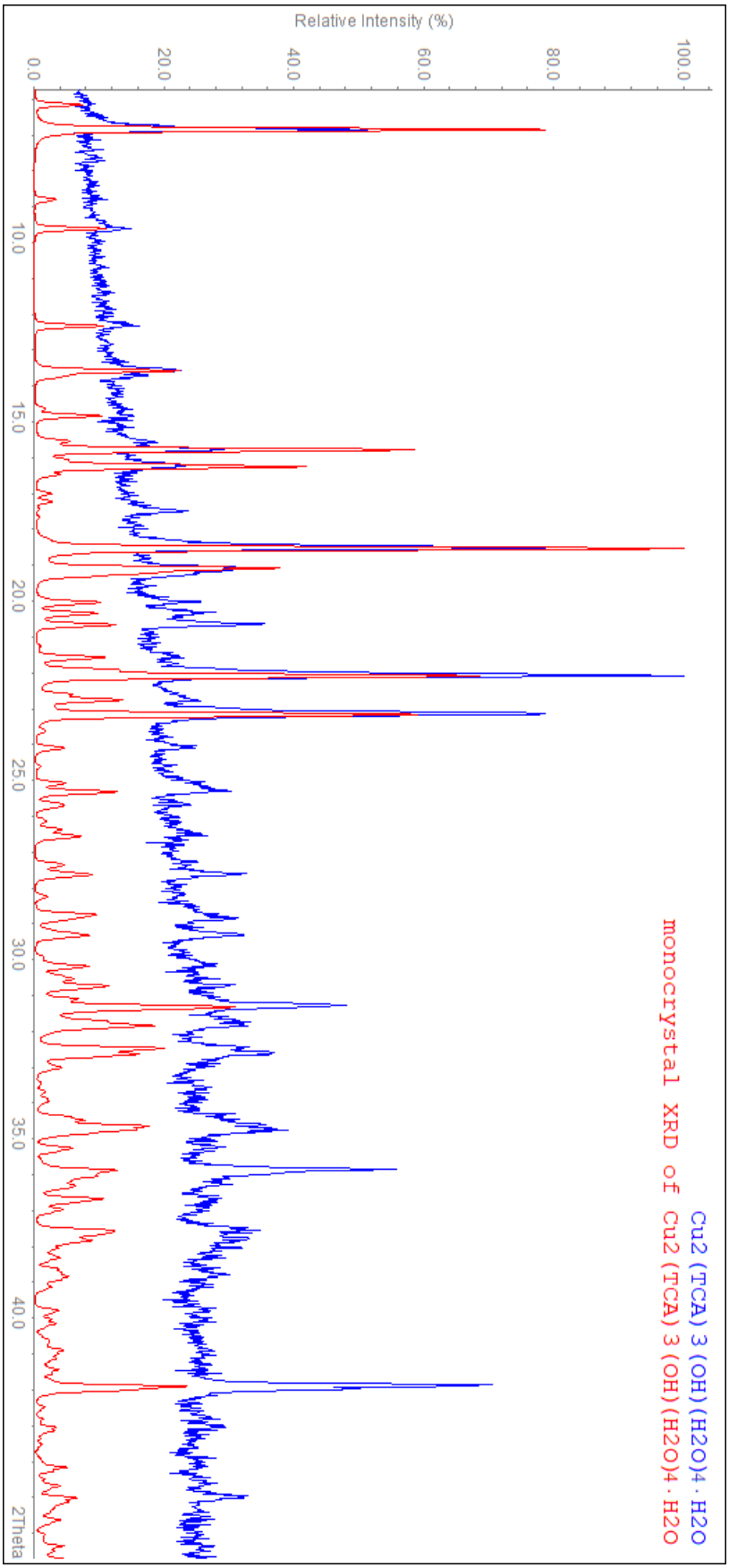


Figure S4. PXRD data for **2** (blue) and its theoretical pattern (red).

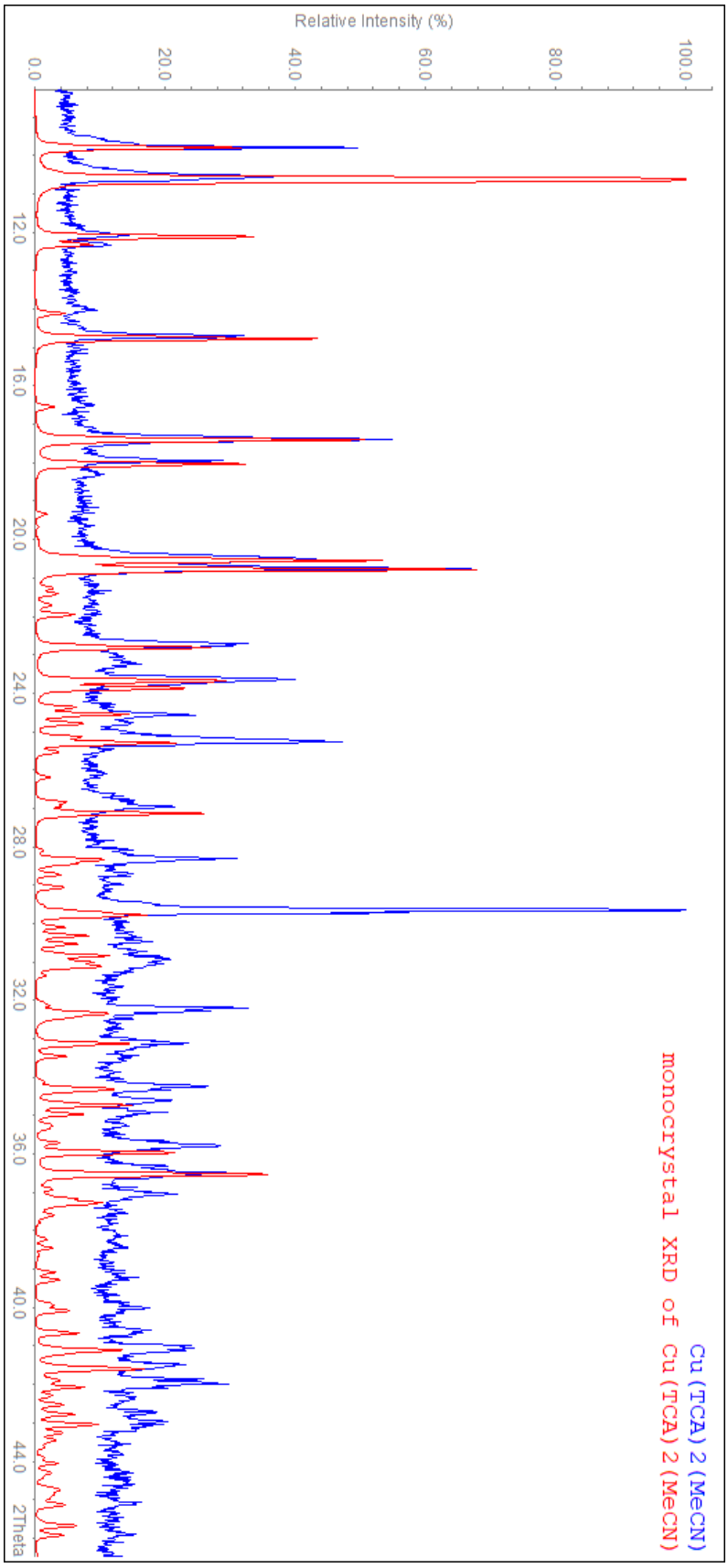
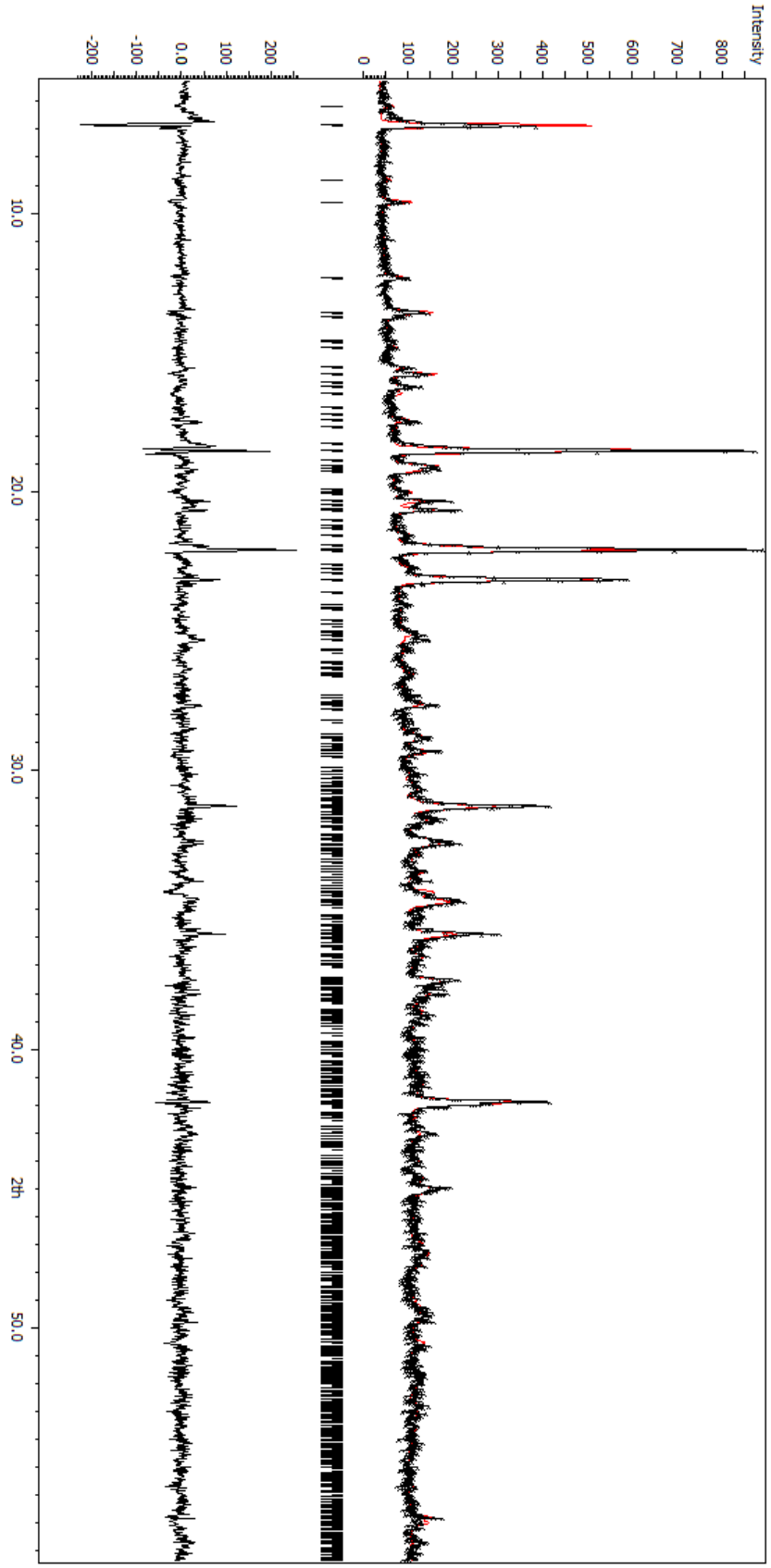


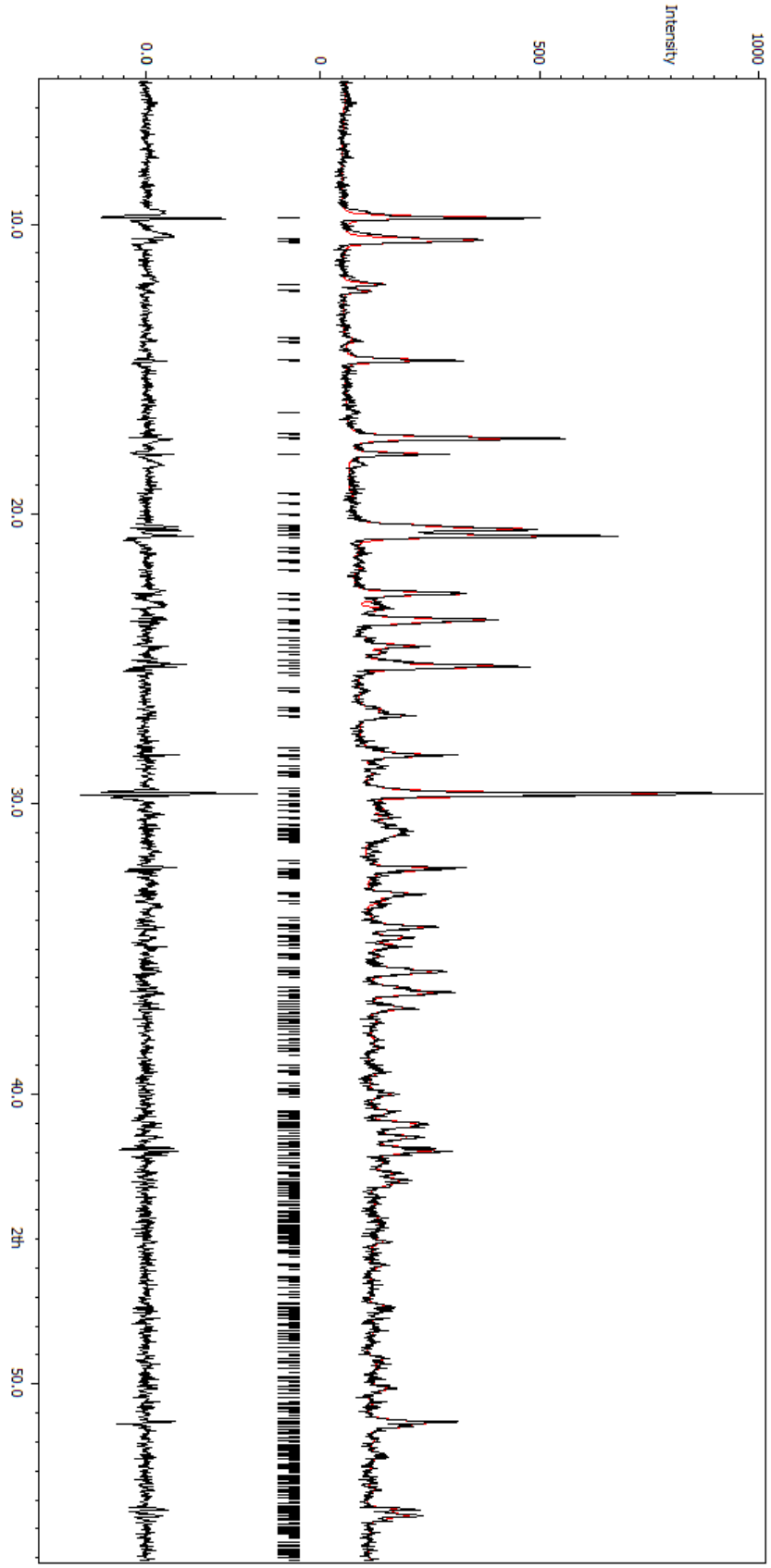
Figure S5. Profile analysis for **1** was carried out using JANA software.[S12]



Cell parameters: 12.9617 6.1069 28.8612 90.000 95.012 90.000 Volume: 2275.8

Centrosymmetric space group: $P2_1/c$ Number: 14 GOF = 1.41 R_p = 10.40 wR_p = 13.59

Figure S6. Profile analysis for **2.**



Cell parameters: 8.8720 9.2161 9.4752 72.343 86.609 71.050 Volume: 697.6

Centrosymmetric space group: P-1 Number: 2 GOF = 1.53 R_p = 10.82 wR_p = 13.97

Figure S7. SEM image (*top*) and photographs (*bottom*) of **1**.

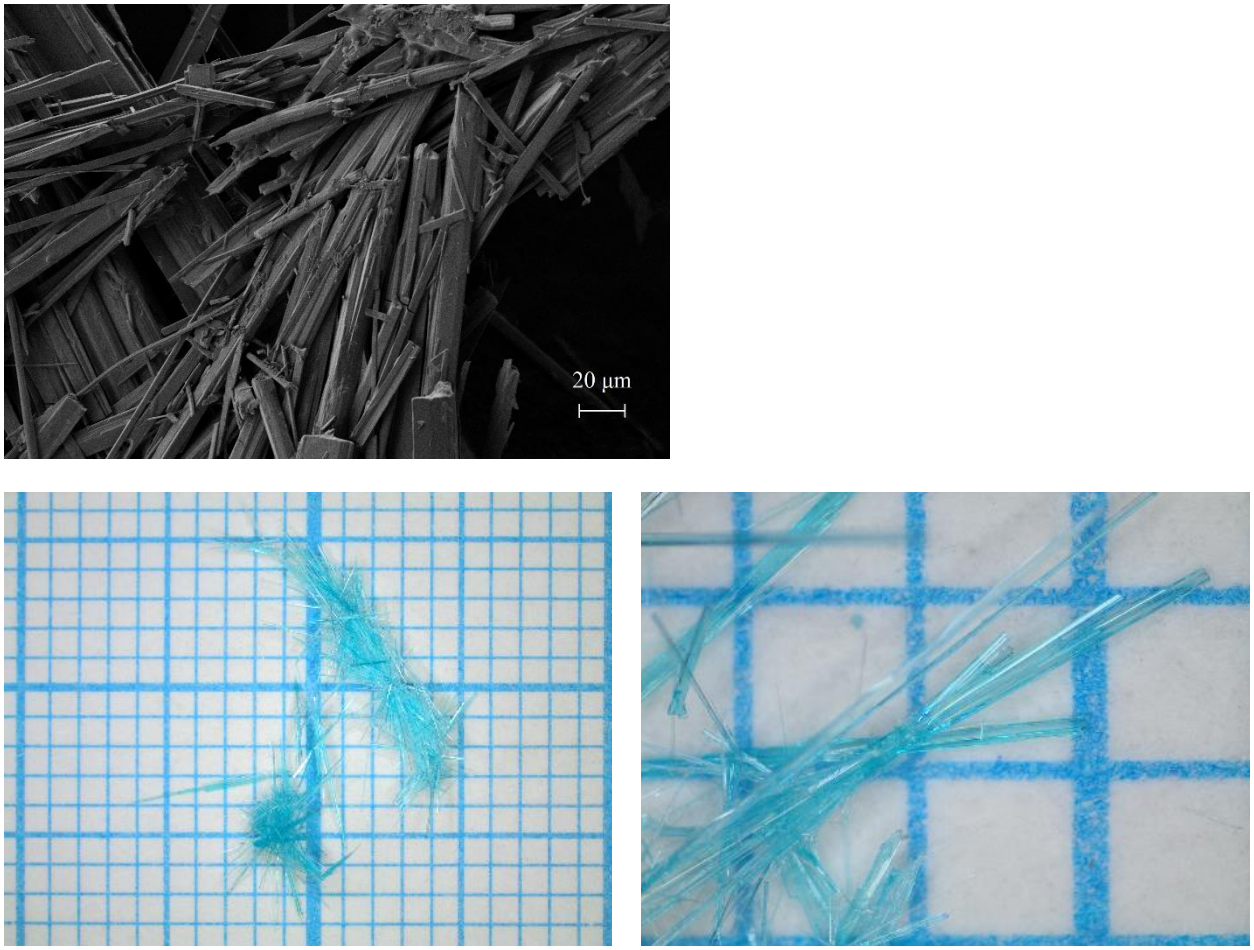
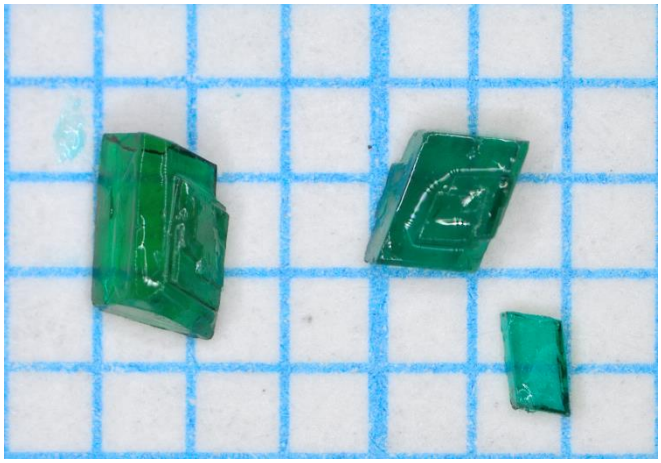


Figure S8. Photograph of **2**.



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