

Supplementary Information

Advancement and Stabilization of Copper(II) Azide by the Use of Triazole- and Tetrazole Ligands

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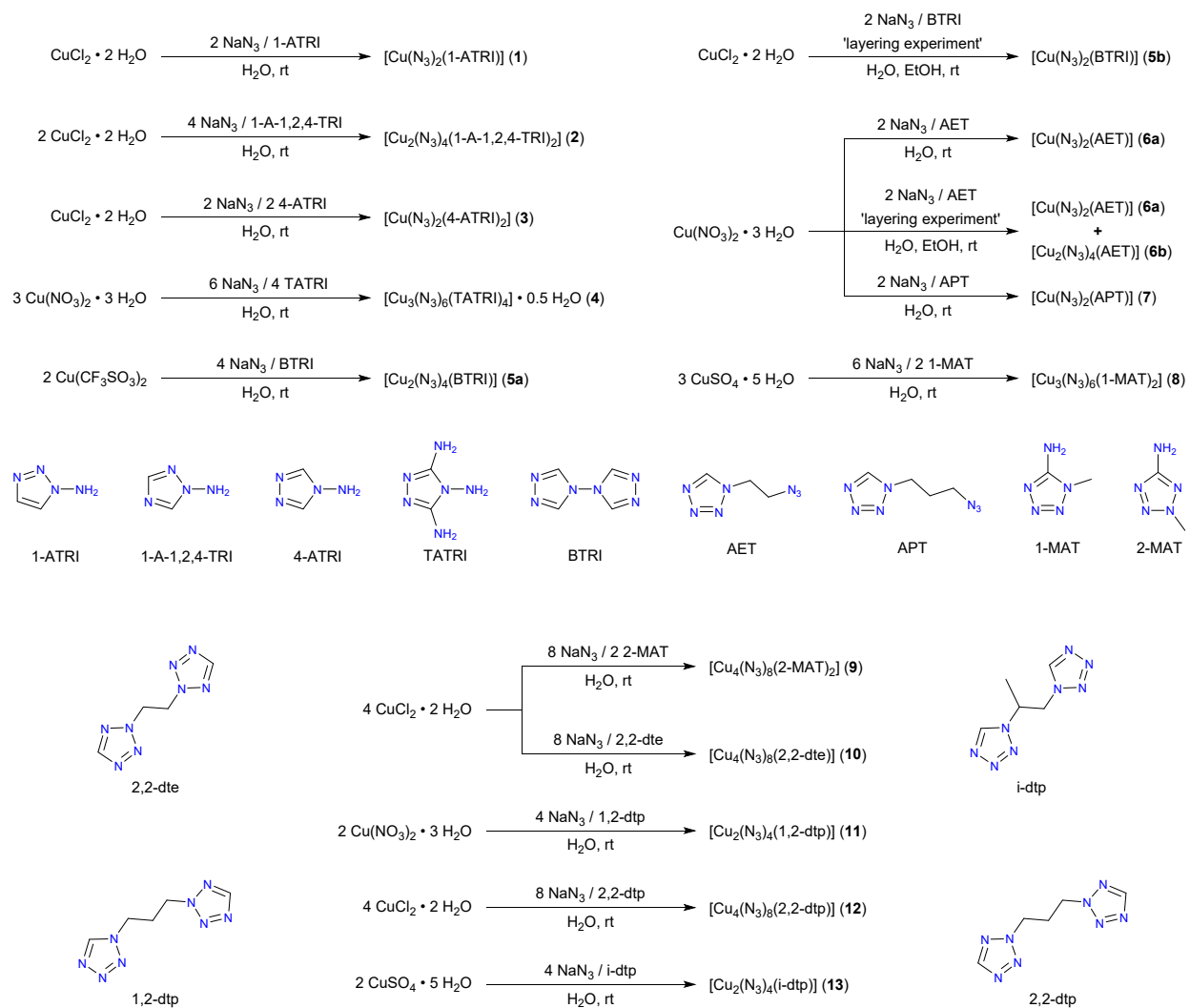
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1. Compounds Overview



2. IR Spectroscopy of 1, 3–7, 9–13

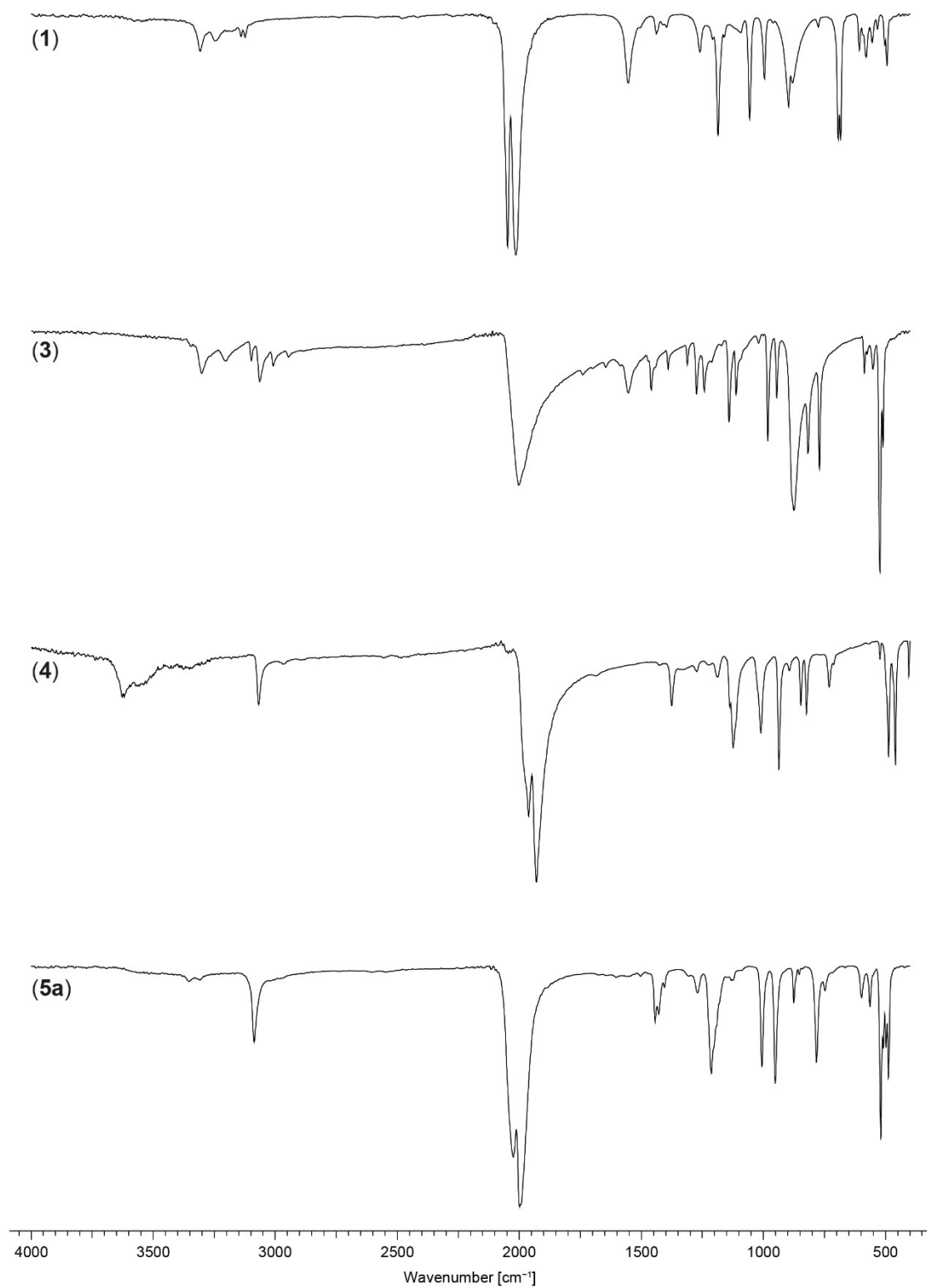


Figure S1. IR spectra of the coordination compounds **1**, **3**, **4**, and **5a**.

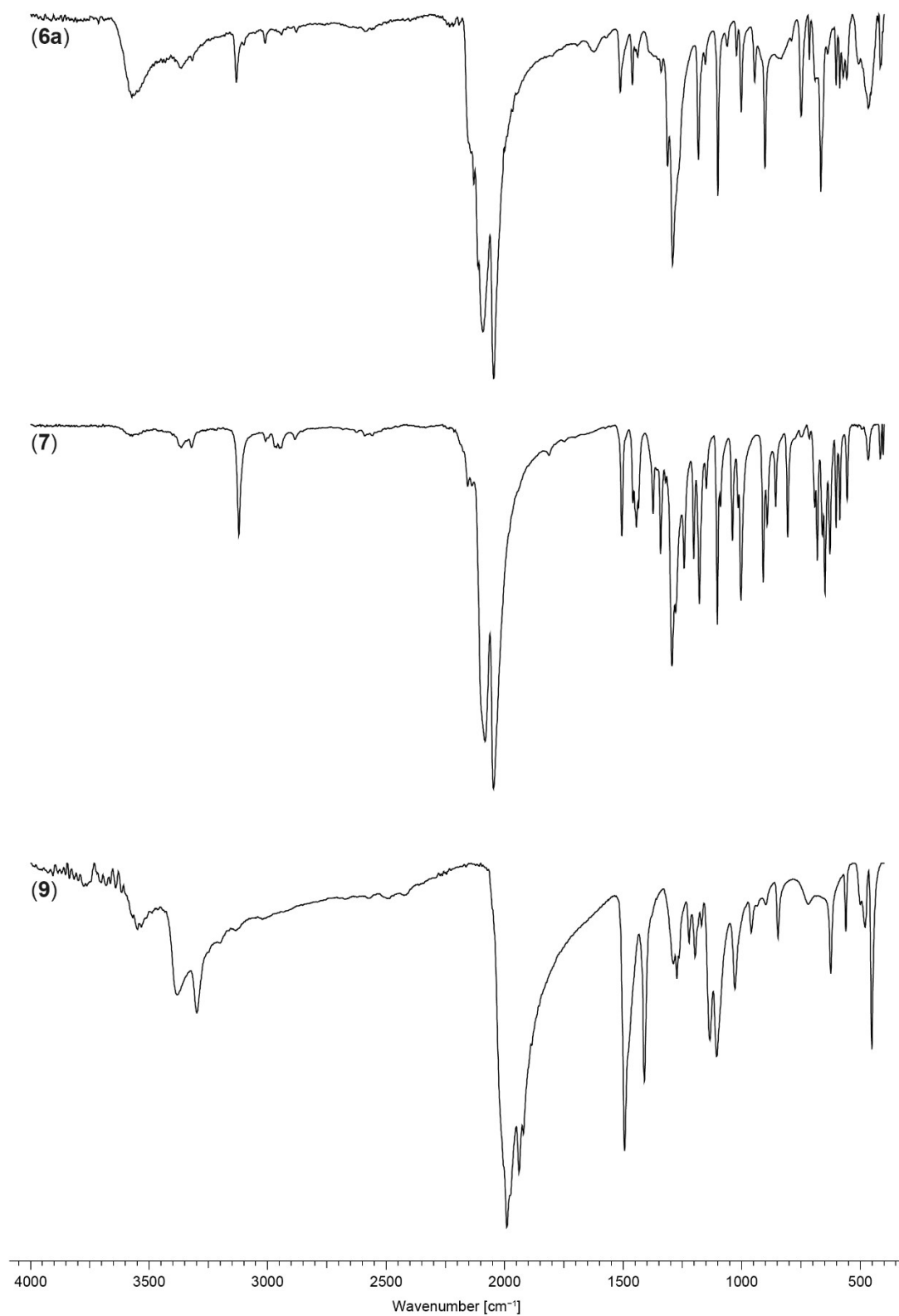


Figure S2. IR spectra of the complexes **6a**, **7**, and **9**.

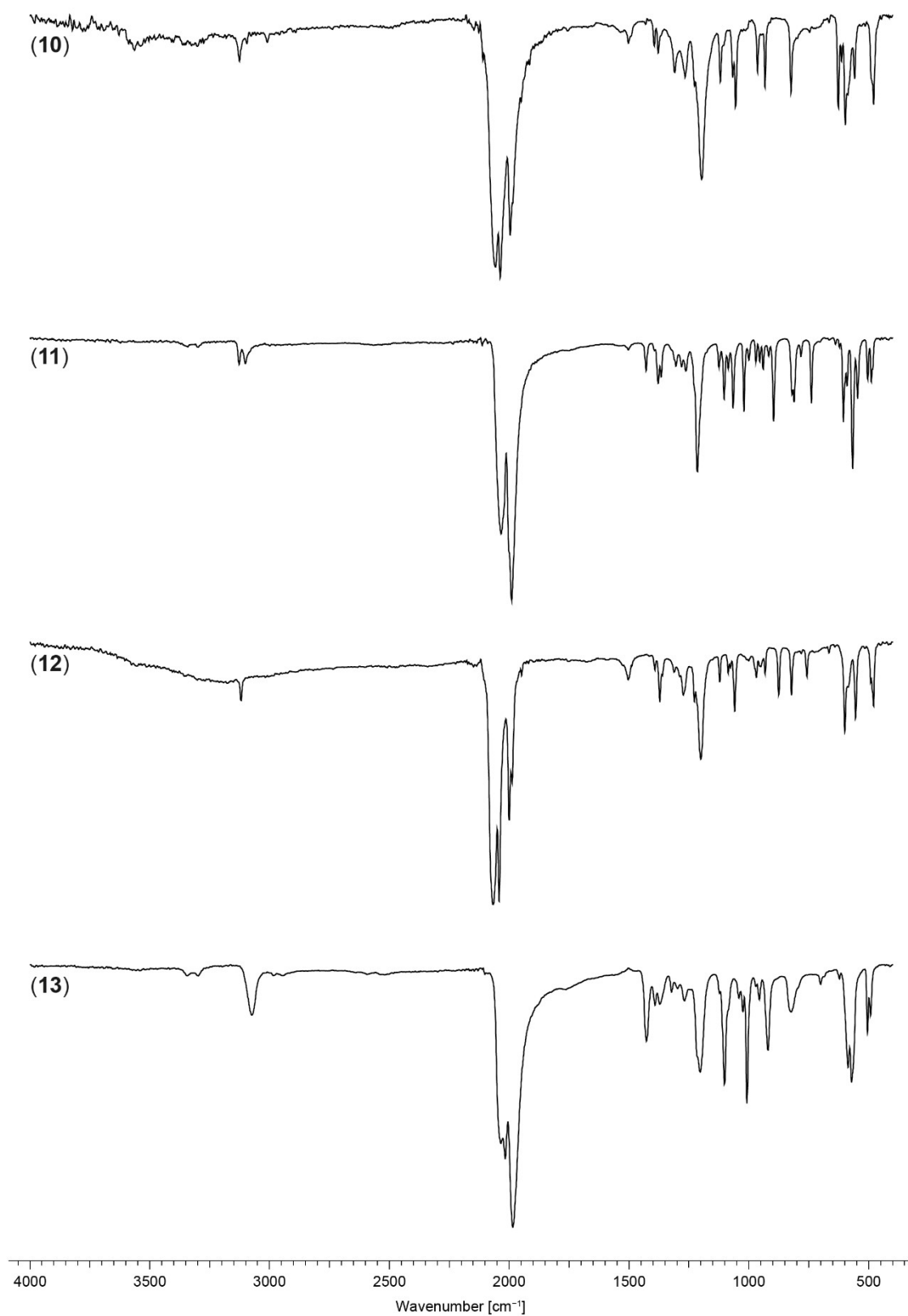


Figure S3. IR spectra of the ECCs **10–13**.

3. X-Ray-Diffraction

For all crystalline compounds, an Oxford Xcalibur3 diffractometer with a CCD area detector or Bruker D8 Venture TXS diffractometer equipped with a multilayer monochromator, a Photon 2 detector and a rotating-anode generator were employed for data collection using Mo- K_{α} radiation ($\lambda = 0.7107 \text{ \AA}$). On the Oxford device, data collection and reduction were carried out using the CrysAlis PRO software.^{S1} On the Bruker diffractometer, the data were collected with the Bruker Instrument Service v3.0.21, the data reduction was performed using the SAINT V8.18C software (Bruker AXS Inc., 2011). The structures were solved by direct methods (SIR-92,^{S2} SIR-97,^{S3,S4} SHELXS-97^{S5,S6} or SHELXT^{S7}) and refined by full-matrix least-squares on F^2 (SHELXL^{S5,S6}) and finally checked using the PLATON software^{S8} integrated in the WinGX^{S9} or Olex2^{S10} software suite. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. The absorptions were corrected by a SCALE3 ABSPACK or SADABS Bruker APEX3 multi-scan method.^{S11,S12} All DIAMOND4 plots are shown with thermal ellipsoids at the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius.

X-ray powder experiments were performed on a Gunier diffractometer (Huber G644) with Mo- $K_{\alpha 1}$ radiation ($\lambda = 0.7093 \text{ \AA}$, quartz monochromator) in Lindemann capillaries (0.7 mm diameter). The angle calibration was performed with electronic grade germanium. In the 2θ range between 4° and 34° with an increment of 0.04° , 750 data points were collected with a counting rate of 10 s for each increment. The Rietveld parameters were analyzed with the program FullProf.^{S13}

3.1 Single Crystal X-Ray-Diffraction

Table S1. Crystallographic data of the coordination compounds **1–4**.

	1	2	3	4
Formula	C ₂ H ₄ CuN ₁₀	C ₂ H ₄ Cu ₂ N ₁₆	C ₄ H ₈ CuN ₁₄	C ₈ H ₂₆ Cu ₃ N ₄₂ O
FW [g mol ⁻¹]	231.70	379.29	315.79	917.33
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> –1	<i>P</i> –1	<i>P</i> –1
Color / Habit	Brown rod	Brown block	Green needle	Green block
Size [mm]	0.02 x 0.03 x 0.10	0.05 x 0.20 x 0.25	0.08 x 0.14 x 0.39	0.04 x 0.06 x 0.08
<i>a</i> [Å]	3.4264(1)	5.7400(7)	5.3987(4)	9.2469(17)
<i>b</i> [Å]	14.7560(5)	9.6530(13)	6.9250(6)	9.826(1)
<i>c</i> [Å]	14.5974(5)	11.1290(14)	7.9095(5)	10.3622(19)
α [°]	90	73.371(12)	114.207(7)	109.261(15)
β [°]	95.029(1)	79.264(11)	92.421(5)	96.057(15)
γ [°]	90	74.775(12)	93.172(7)	115.091(15)
<i>V</i> [Å ³]	735.20(4)	565.98(13)	268.61(4)	771.1(3)
<i>Z</i>	4	2	1	1
$\rho_{\text{calc.}}$ [g cm ⁻³]	2.093	2.226	1.952	1.975
μ [mm ⁻¹]	2.939	3.781	2.050	2.140
<i>F</i> (000)	460	372	159	463
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
<i>T</i> [K]	100	143	143	123
θ Min-Max [°]	2.8, 26.3	4.4, 26.0	4.6, 26.0	3.6, 26.4
Dataset	–4: 4; 0: 18; 0: 18	–5: 7; –11: 11; –13: 13	–6: 6; –8: 6; –9: 9	–10: 11; –12: 12; –12: 9
Reflections collected	1517	4087	1934	4240
Independent refl.	1517	2206	1057	3113
<i>R</i> _{int}	0.000	0.037	0.021	0.036
Observed reflections	1456	1712	1007	2313
Parameters	119	189	96	296
<i>R</i> ₁ (obs) ^[a]	0.0324	0.0343	0.0269	0.0506
<i>wR</i> ₂ (all data) ^[b]	0.0950	0.0794	0.0694	0.1157
GooF ^[c]	1.27	1.01	1.12	1.03
Resd. Dens. [e Å ⁻³]	–0.49, 0.46	–0.52, 0.65	–0.40, 0.53	–0.67, 0.74
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Device type	Bruker D8 Venture TXS	Oxford Xcalibur3	Oxford Xcalibur3	Oxford Xcalibur3
CCDC	2081740	2084455	2081730	2081737

a) $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; b) $wR_2 = [\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma (w(F_o^2)^2)]^{1/2}$; $w = [\sigma^2(F_o^2) + (xP)^2 + yP]^{-1}$ and $P = (F_o^2 + 2F_c^2) / 3$; c) GooF = $\{\Sigma [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$ (*n* = number of reflections; *p* = total number of parameters).

Table S2. Crystallographic data of the compounds **5b–7**.

	5b	6a	6b	7
Formula	C ₄ H ₄ CuN ₁₂	C ₃ H ₅ CuN ₁₃	C ₃ H ₅ Cu ₂ N ₁₉	C ₄ H ₇ CuN ₁₃
FW [g mol ⁻¹]	283.73	286.74	434.34	300.77
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>I</i> 2/ <i>a</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
Color / Habit	Red platelet	Brown plate	Brown rod	Brown platelet
Size [mm]	0.01 x 0.04 x 0.09	0.02 x 0.15 x 0.15	0.02 x 0.05 x 0.47	0.01 x 0.08 x 0.10
<i>a</i> [Å]	13.4279(5)	10.6755(7)	5.6349(3)	16.3042(14)
<i>b</i> [Å]	6.3343(2)	6.3077(5)	26.5998(16)	6.2946(5)
<i>c</i> [Å]	10.7437(4)	28.327(2)	9.6251(7)	10.6903(9)
α [°]	90	90	90	90
β [°]	92.645(1)	94.465(7)	105.208(7)	106.287(3)
γ [°]	90	90	90	90
<i>V</i> [Å ³]	912.85(6)	1901.7(2)	1392.16(16)	1053.10(15)
<i>Z</i>	4	8	4	4
$\rho_{\text{calc.}}$ [g cm ⁻³]	2.065	2.003	2.072	1.897
μ [mm ⁻¹]	2.394	2.302	3.094	2.083
<i>F</i> (000)	564	1144	856	604
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
<i>T</i> [K]	173	143	143	109
θ Min-Max [°]	3.0, 26.0	4.1, 32.4	4.4, 26.4	3.5, 28.3
Dataset	–16: 16; –7: 7; –13: 13	–15: 15; –9: 9; –41: 41	–7: 6; –32: 33; –11: 12	0: 21; –8: 0; –14: 13
Reflections collected	15502	10094	11589	2066
Independent refl.	1797	3170	2821	2066
<i>R</i> _{int}	0.033	0.054	0.059	0.000
Observed reflections	1632	2284	2128	1905
Parameters	154	154	218	164
<i>R</i> ₁ (obs) ^[a]	0.0200	0.0404	0.0343	0.0393
<i>wR</i> ₂ (all data) ^[b]	0.0510	0.0879	0.0701	0.0787
GooF ^[c]	1.08	1.07	1.01	1.16
Resd. Dens. [e Å ⁻³]	–0.24, 0.27	–0.53, 1.25	–0.41, 0.60	–0.52, 0.74
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Device type	Bruker D8 Venture TXS	Oxford Xcalibur3	Oxford Xcalibur3	Bruker D8 Venture TXS
CCDC	2081736	2081733	2081735	2081738

a) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; b) $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$; $w = [\sigma^2(F_o^2) + (xP)^2 + yP]^{-1}$ and $P = (F_o^2 + 2F_c^2) / 3$; c) GooF = $\{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$ (*n* = number of reflections; *p* = total number of parameters).

Table S3. Crystallographic data of the complexes **8**, **9**, **10**, and **12**.

	8	9	10	12
Formula	C ₄ H ₁₀ Cu ₃ N ₂₈	C ₂ H ₅ Cu ₂ N ₁₇	C ₄ H ₆ Cu ₄ N ₃₂	C ₅ H ₈ Cu ₄ N ₃₂
FW [g mol ⁻¹]	641.02	394.31	756.50	770.59
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>C</i> 2/ <i>c</i>
Color / Habit	Red platelet	Red rod	Brown needle	Brown needle
Size [mm]	0.01 x 0.05 x 0.08	0.01 x 0.02 x 0.10	0.03 x 0.04 x 0.19	0.02 x 0.25 x 0.50
<i>a</i> [Å]	6.2454(4)	14.7855(6)	5.5720(6)	18.2752(11)
<i>b</i> [Å]	8.5723(5)	5.6009(2)	9.4130(12)	5.5456(3)
<i>c</i> [Å]	10.1414(6)	14.8579(6)	11.5810(12)	24.0470(13)
α [°]	91.435(2)	90	102.066(10)	90
β [°]	106.685(2)	103.424(2)	91.440(9)	100.556(5)
γ [°]	102.203(2)	90	105.227(11)	90
<i>V</i> [Å ³]	506.20(5)	1196.80(8)	571.08(12)	2395.9(2)
<i>Z</i>	1	4	2	4
$\rho_{\text{calc.}}$ [g cm ⁻³]	2.103	2.188	2.200	2.136
μ [mm ⁻¹]	3.189	3.583	3.747	3.574
<i>F</i> (000)	317	776	370	1512
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
<i>T</i> [K]	293	100	143	123
θ Min-Max [°]	3.1, 26.0	2.2, 26.0	4.2, 26.0	4.3, 26.0
Dataset	-7: 7; -10: 10; -12: 12	-18: 18; -6: 6; -18: 18	-6: 6; -8: 11; -12: 14	-15: 22; -6: 6; -29: 29
Reflections collected	8877	11334	4119	9212
Independent refl.	1989	2350	2235	2347
<i>R</i> _{int}	0.027	0.044	0.056	0.045
Observed reflections	1801	2018	1412	1894
Parameters	161	199	181	186
<i>R</i> ₁ (obs) ^[a]	0.0203	0.0263	0.0485	0.0329
<i>wR</i> ₂ (all data) ^[b]	0.0524	0.0910	0.1012	0.0829
GooF ^[c]	1.06	1.22	0.97	1.08
Resd. Dens. [e Å ⁻³]	-0.28, 0.26	-0.45, 0.48	-0.67, 1.49	-0.72, 0.77
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Device type	Bruker D8 Venture TXS	Bruker D8 Venture TXS	Oxford Xcalibur3	Oxford Xcalibur3
CCDC	2081732	2081739	2081734	2081731

a) $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; b) $wR_2 = [\Sigma \{w(F_o^2 - F_c^2)^2\} / \Sigma \{w(F_o^2)^2\}]^{1/2}$; $w = [\sigma^2(F_o^2) + (xP)^2 + yP]^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$; c) GooF = $\{\Sigma [w(F_o^2 - F_c^2)^2] / (n-p)\}^{1/2}$ (*n* = number of reflections; *p* = total number of parameters).

3.2 Powder Diffraction

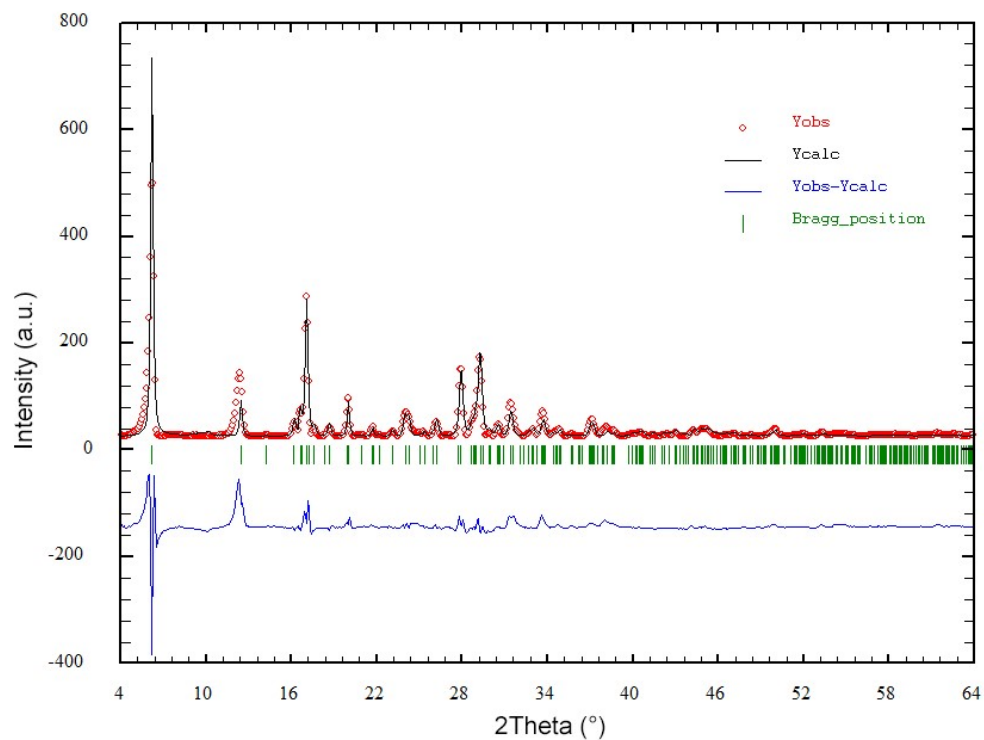


Figure S4. Powder XRD of $[\text{Cu}(\text{N}_3)_2(\text{AET})]$ (**6a**).

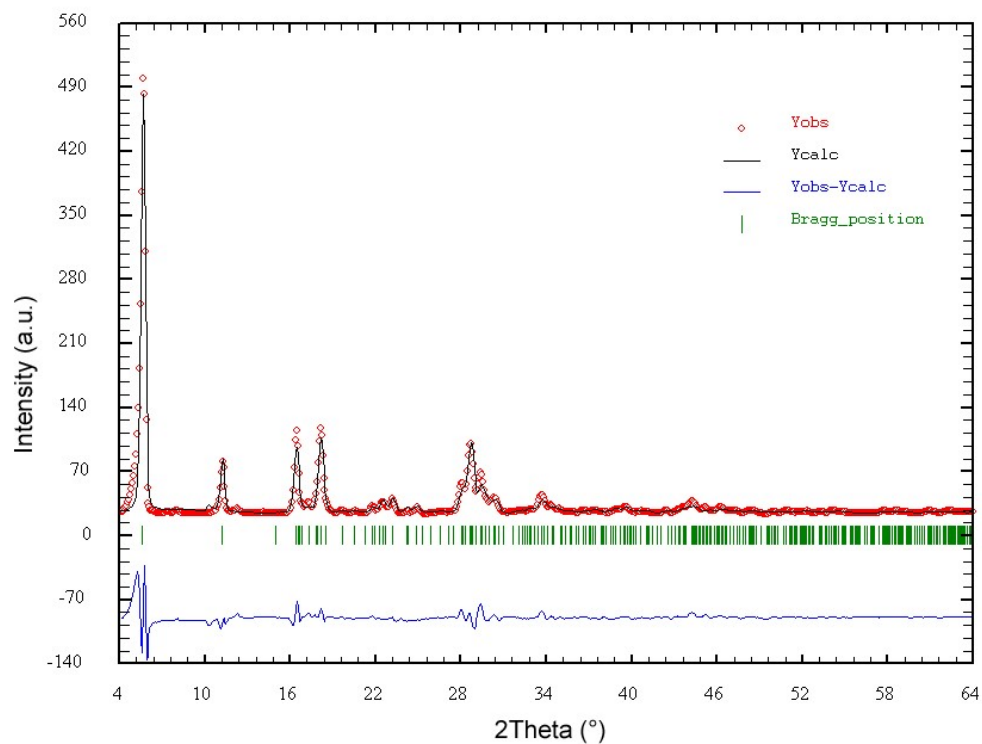


Figure S5. Powder XRD of $[\text{Cu}(\text{N}_3)_2(\text{APT})]$ (**7**).

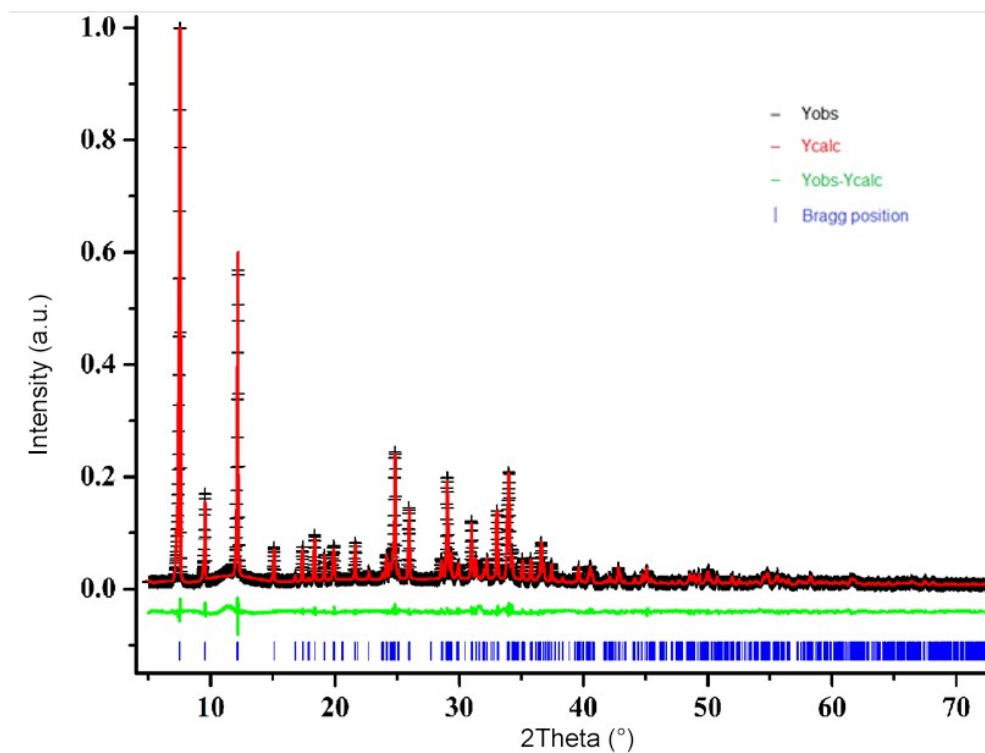


Figure S6. Powder XRD of $[\text{Cu}_4(\text{N}_3)_8(2\text{-MAT})_2]$ (9).

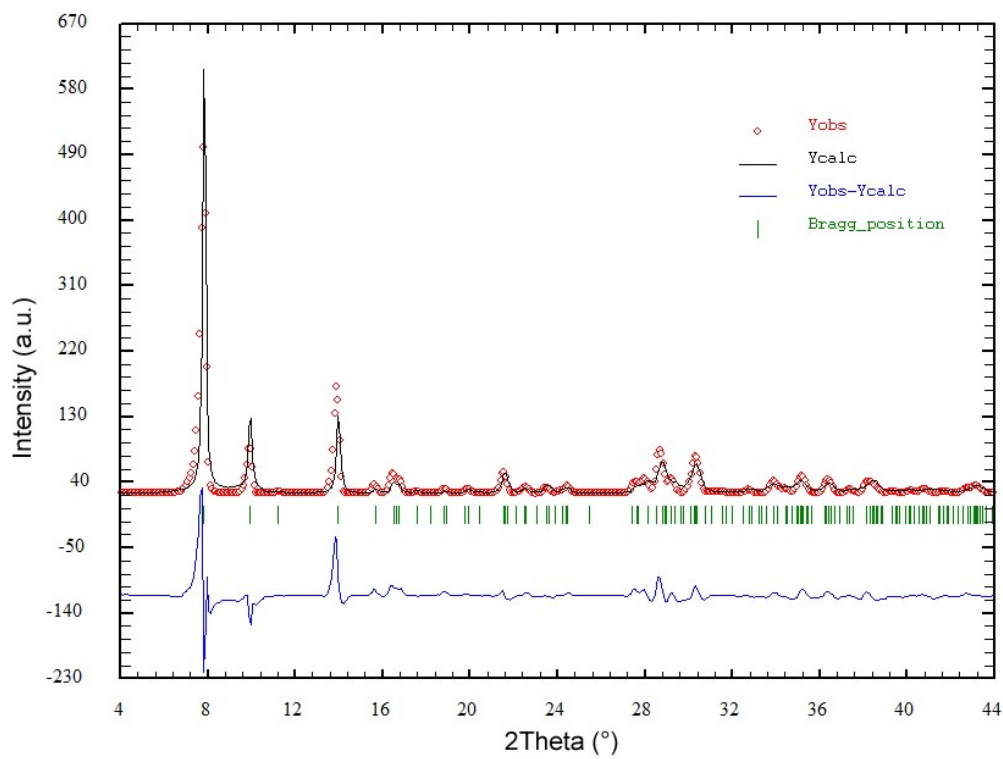


Figure S7. Powder XRD of $[\text{Cu}_4(\text{N}_3)_8(2,2\text{-dte})]$ (10).

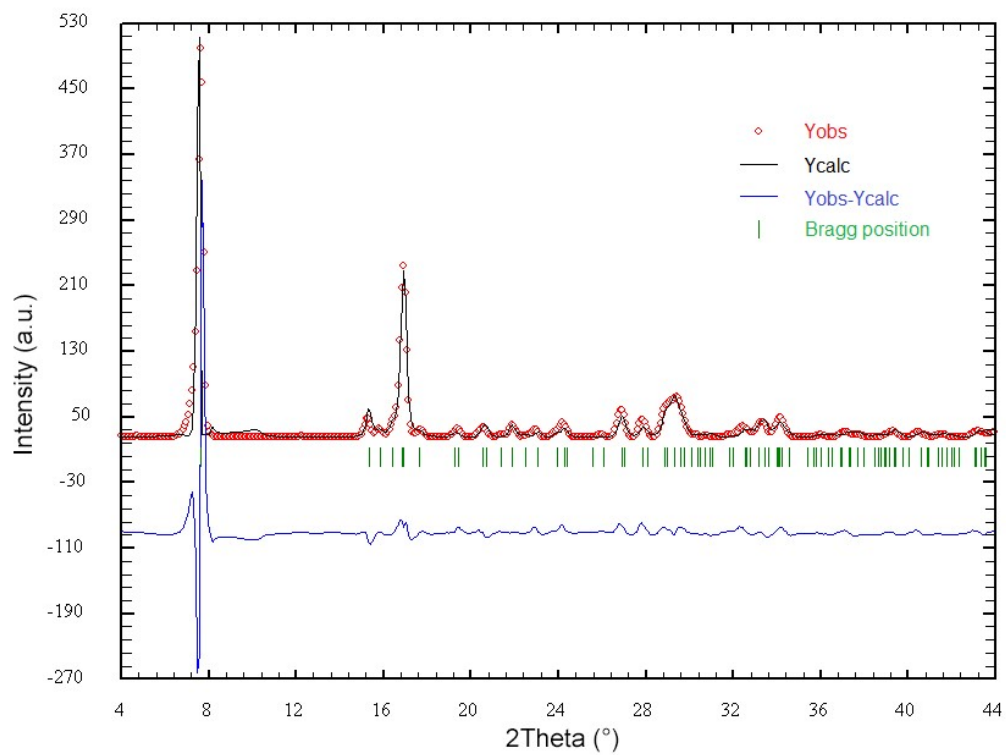


Figure S8. Powder XRD of $[\text{Cu}_2(\text{N}_3)_4(1,2\text{-dtp})]$ (11).

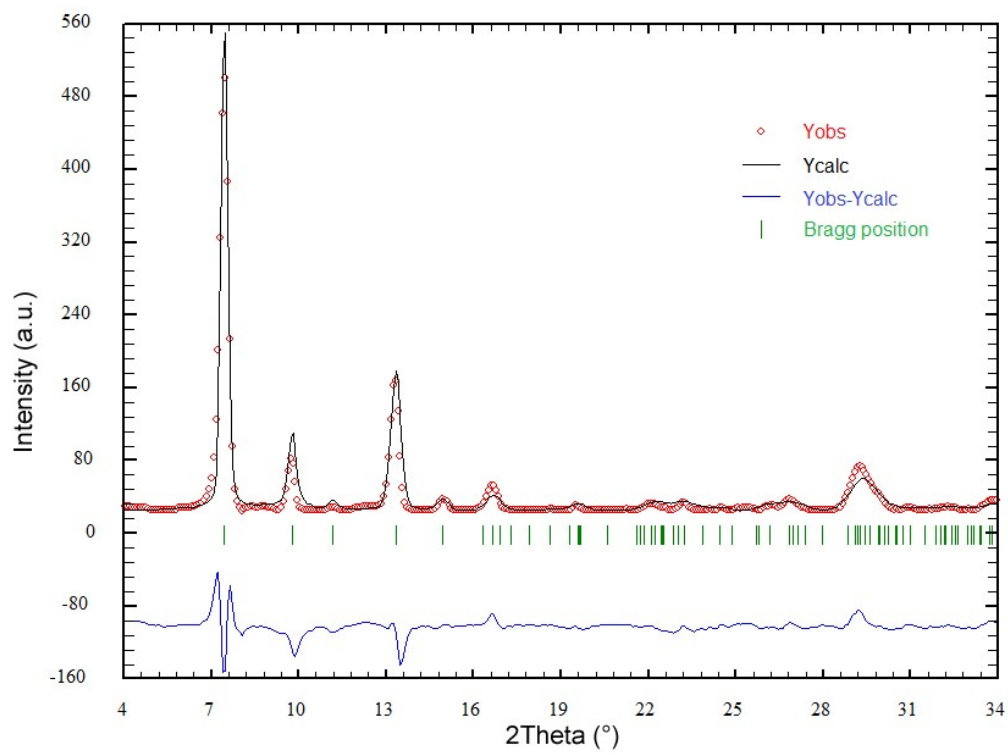


Figure S9. Powder XRD of $[\text{Cu}_4(\text{N}_3)_8(2,2\text{-dtp})]$ (12).

4. DTA Plots of 1, 3–7, 9–13

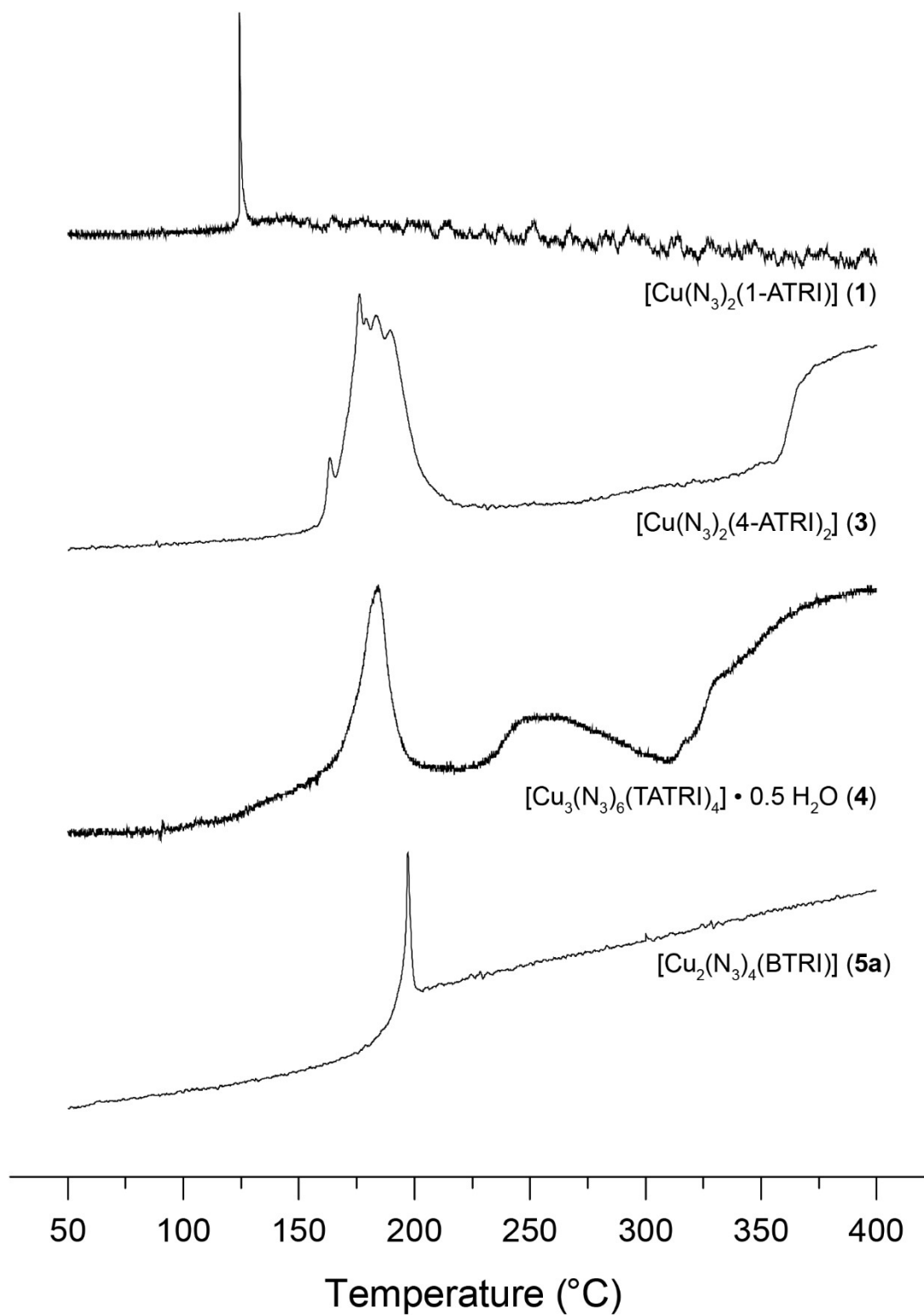


Figure S10. DTA plots of the ECCs **1**, **3**, **4**, and **5a**.

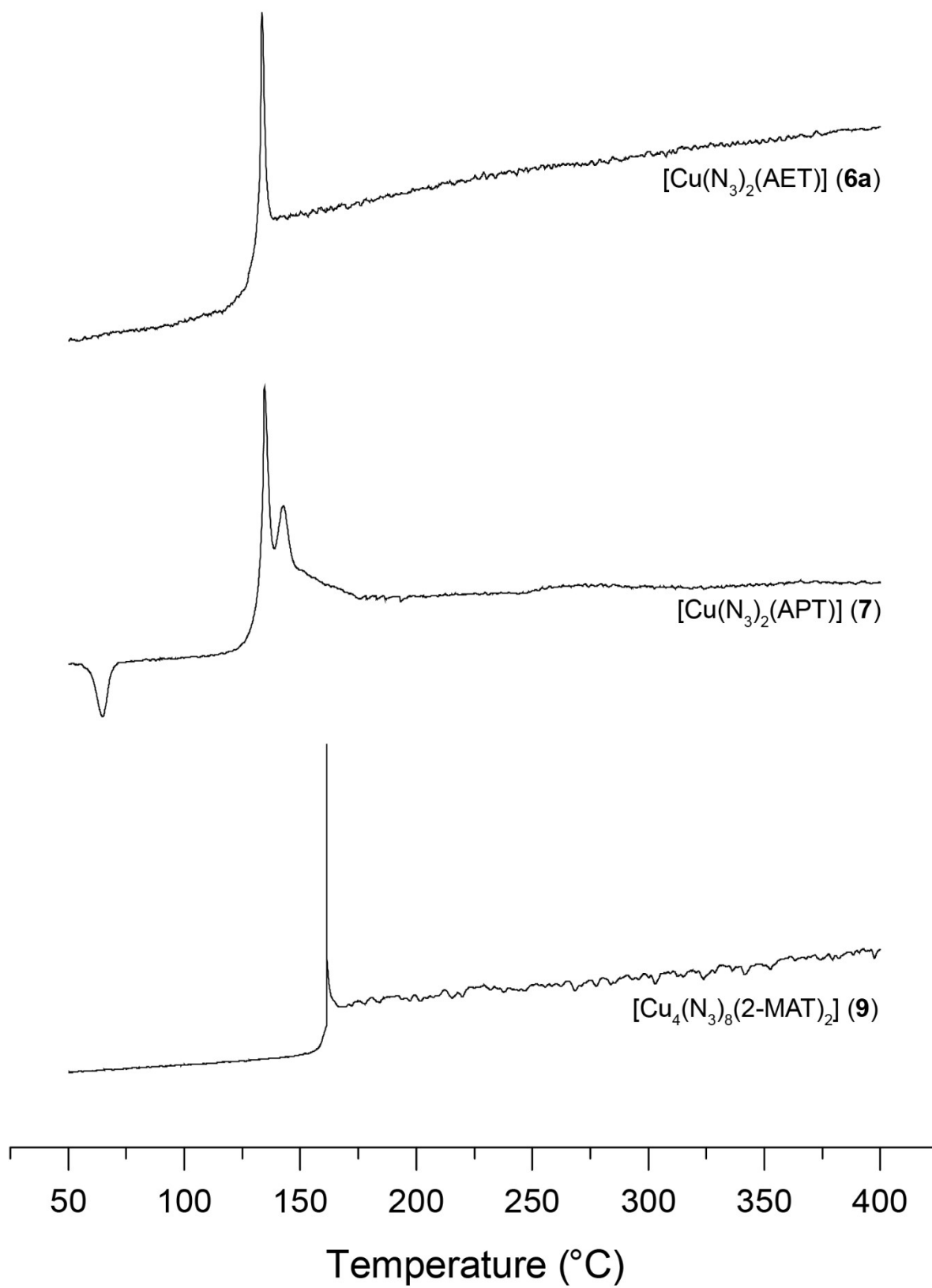


Figure S11. DTA plots of the coordination compounds **6a**, **7**, and **9**.

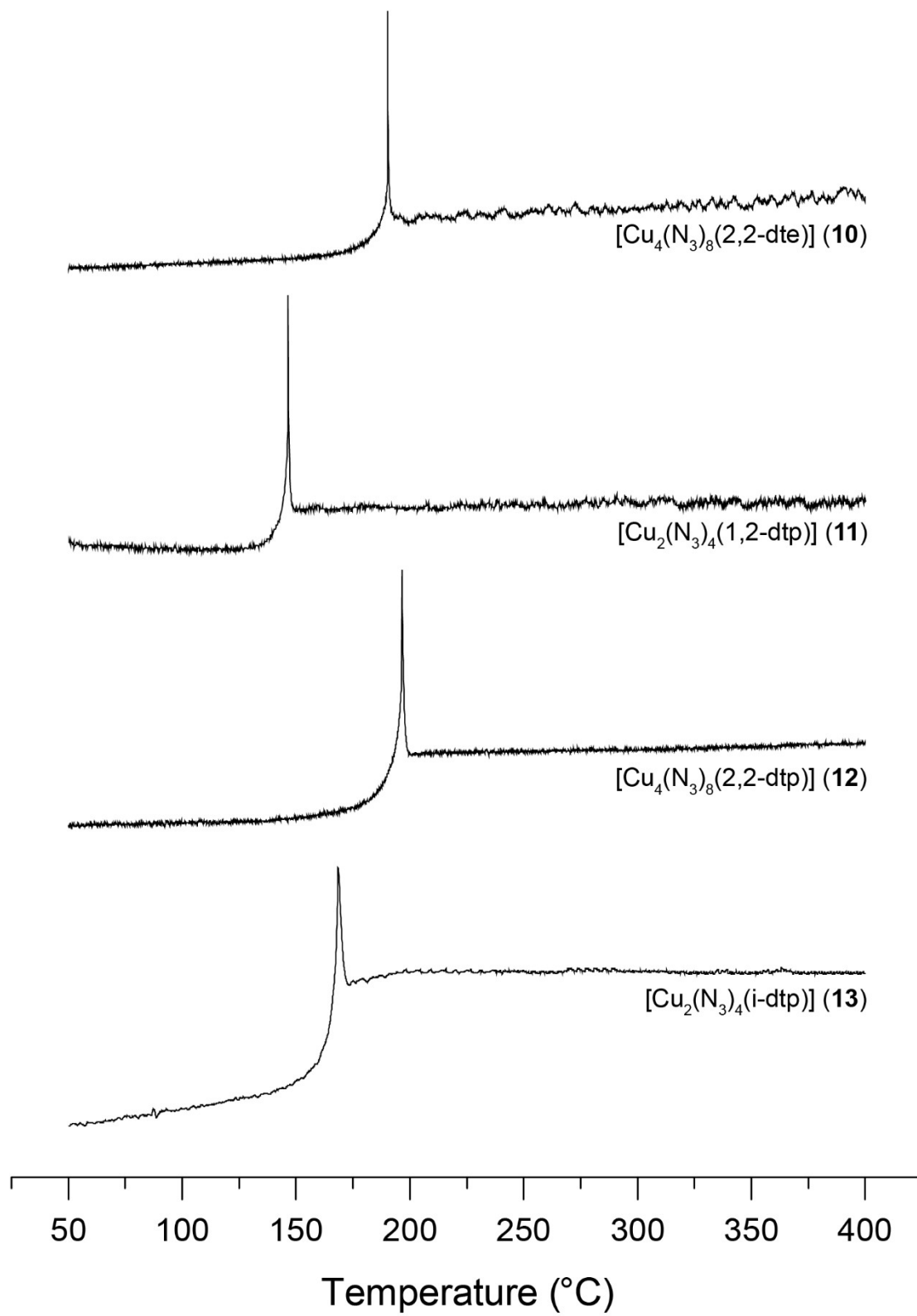


Figure S12. DTA plots of the complexes **10–13**.

5. Detonation Velocity Estimations

The room temperature densities used for calculation of the detonation velocity were either obtained by gas pycnometry (**5a**: 2.252 g cm⁻³, **11**: 2.064 g cm⁻³, **13**: 2.034 g cm⁻³) or by recalculation of the the low temperature densities, obtained by X-ray diffraction experiments (**6a**: 1.957 g cm⁻³, **9**: 2.125 g cm⁻³, **10**: 2.150 g cm⁻³ and **12**: 2.081 g cm⁻³). Detonation velocities were calculated according to an increment method, adapted for ECC by Ilyushin.^{S14} Similar to pyrotechnical mixtures, the respective ECC was divided into an explosive part (anion, ligand) and an inactive ultratispersed metal additive (copper). The active part was further divided into chemical bonds and structural fragments. Corresponding increment values can be found in the literature.^{S15} Some of the values are dependent on the hydrogen and oxygen content of the coordination compound, the summarized values for each fragment are listed in Table S4.

Table S4. Increment values of the used fragments.

Fragment	F_i
AET	436.4
BTRI	351.5
2,2-dte	470.0
1,2-dtp	482.5
2,2-dtp	482.5
i-dtp	477.2
2-MAT	271.5
N ₃ ⁻	190.3

6. Experimental Part & General Methods

All chemicals and solvents were employed as received (Sigma-Aldrich, Fluka, Acros, ABCR). Endothermic and exothermic events of the described compounds, which indicate melting, loss of aqua ligands, crystal water or decomposition, are given as the extrapolated onset temperatures. The samples were measured in a range of 25–400 °C at a heating rate of 5 °C min⁻¹ through differential thermal analysis (DTA) with an OZM Research DTA 552-Ex. Infrared spectra were measured with neat samples on a Perkin-Elmer BXII FT-IR system with a Smith DuraSampler IR II diamond ATR. Determination of the carbon, hydrogen and nitrogen contents was carried out by combustion analysis using an Elementar Vario El (nitrogen values determined are often lower than the calculated ones' due to their explosive behavior). Impact sensitivity tests were carried out according to STANAG 4489^{S18} with a modified instruction^{S19} using a BAM (Bundesanstalt für Materialforschung) drophammer.^{S18} Friction sensitivity tests were carried out according to STANAG 4487^{S19} with a modified instruction^{S20} using the BAM friction tester.^{S18,S21} The classification of the tested compounds results from the "UN Recommendations on the Transport of Dangerous Goods".^{S22,S23} Additionally, all compounds were tested upon the sensitivity toward electrical discharge using the OZM Electric Spark XSpark10 device.^{S22} Hot plate and hot needle tests were performed in order to evaluate the potential initiation capability of selected complexes. The samples were fixed on a copper plate underneath adhesive tape and initiated by a red-hot needle. Strong deflagration or detonation of the compound usually indicates a valuable primary explosive. The safe and straightforward hot plate test only shows the behavior of the unconfined sample toward fast heating on a copper plate. It does not necessarily allow any conclusions on a compound's capability as a suitable primary explosive. The laser initiation experiments were performed with a 45 W InGaAs laser diode operating in the single-pulsed mode. The diode is attached to an optical fiber with a core diameter of 400 µm and a cladding diameter of 480 µm. The optical fiber is connected via a SMA type connector directly to the laser and to a collimator. This collimator is coupled to an optical lens, which was positioned in its focal

distance ($f = 29.9$ mm) to the sample. The lens is shielded from the explosive by a sapphire glass. Approximately 15 mg of the carefully pestled compound to be investigated was filled into a transparent plastic cap (PC), pressed with a pressure force of 1 kN and sealed by a UV-curing adhesive. The confined samples were irradiated at a wavelength of 915 nm, a voltage of 4 V, a current of 7–8 A and pulse lengths of 0.1–15 ms. The combined currents and pulse lengths result in an energy output of 0.17–25.5 mJ.

The obtained coordination compounds were washed with cold ethanol when stated, dried overnight in air, and used for analytics without further purification.

CAUTION! *All investigated compounds are explosive energetic materials, which show extreme sensitivities toward various stimuli (e.g. elevated temperatures, impact, friction or electrostatic discharge). Therefore, proper security precautions (safety glass, face shield, earthed equipment and shoes, leather coat, Kevlar gloves, Kevlar sleeves and ear plugs) have to be applied while synthesizing and handling the described compounds.*

General procedure for the preparation of complexes 1–13:

Stoichiometric amounts for the theoretical synthesis of 0.25 mmol of the coordination compounds were used. Copper(II) chloride dihydrate (**1**, **3**, **9**, **10**, **12**), sulfate pentahydrate (**13**), nitrate trihydrate (**4**, **6a**, **7**, **11**), or triflate (**5a**) and the ligand were stirred mechanically in 7 mL water, the corresponding quantity of sodium azide, dissolved in 1 mL water, was added dropwise within 1 min and the suspension was further stirred for 15 to 60 min. The precipitated complex compounds were filtered off, washed with water (3 x 2 mL) and dried in air.

General procedure for the preparation of single crystals:

Single crystals growth of **1**, **2**, **4**, **5b**, and **6–8**, **10–13** were achieved by overlaying an aqueous solution (8 mL) of sodium azide and the ligand with an ethanolic solution (8 mL) of copper(II) chloride dihydrate, separated by a mixture (4 mL) of water/ethanol (50/50). After 7 to 14 days crystals suitable for X-ray determination were obtained.

[Cu(N₃)₂(1-ATRI)] (**1**)

Complex compound **1** was obtained as dark brown precipitate. Yield: 46.8 mg (0.20 mmol, 81%).

DTA (5 °C min⁻¹) onset: 123 °C (exothermic); IR (ATR, cm⁻¹): ν = 3326 (w), 3267 (w), 3164 (vw), 3148 (vw), 2102 (vs), 2069 (vs), 1621 (w), 1509 (vw), 1483 (vw), 1469 (vw), 1336 (w), 1286 (w), 1264 (m), 1239 (vw), 1174 (vw), 1138 (m), 1079 (w), 1045 (vw), 983 (m), 967 (w), 864 (vw), 785 (m), 776 (m), 701 (w), 674 (w), 650 (w), 629 (vw), 600 (w), 591 (w); EA (C₂H₄CuN₁₀, 231.67): calcd: C 10.37, H 1.74, N 60.46%; found: C 10.40, H 1.81, N 56.77%; BAM drop hammer: 3 J; friction tester: < 5 N; ESD: 5 mJ (at grain size < 100 μ m).

[Cu₂(N₃)₄(1-A-1,2,4-TRI)₂] (**2**)

Single crystals of compound **2** were received according to the general procedure. An elemental analysis pure isolation of the compound was not possible because of side species formation.

[Cu(N₃)₂(4-ATRI)₂] (**3**)

From the reaction mixture, ECC **3** could be isolated as a green powder. Yield: 60.5 mg (0.19 mmol, 77%). Slow evaporation of the mother liquor gave green needle-like crystals within 10 days suitable for X-ray determination.

DTA (5 °C min⁻¹) onset: 161 °C (exothermic); IR (ATR, cm⁻¹): ν = 3321 (w), 3223 (w), 3123 (w), 3090 (w), 3036 (w), 2975 (w), 2058 (s), 1803 (w), 1711 (w), 1621 (w), 1530 (w), 1463 (w), 1386 (w), 1349 (w), 1319 (w), 1289 (w), 1220 (m), 1192 (w), 1102 (vw), 1066 (m), 1030 (w), 962 (s), 906 (m), 860 (m), 681 (w), 670 (vw), 647 (w), 619 (vs), 607 (m); EA (C₄H₈CuN₁₄, 315.75): calcd: C 15.22, H 2.55, N 62.10%; found: C 15.46, H 2.60, N 59.57%; BAM drop hammer: 10 J; friction tester: > 360 N; ESD: 300 mJ (at grain size < 100 μ m).

[Cu₃(N₃)₆(TATRI)₄] • 0.5 H₂O (**4**)

Coordination compound **4** could be isolated as a green powder directly from the reaction solution. Yield: 107.7 mg (0.12 mmol, 47%).

DTA (5 °C min⁻¹) onset: 170 °C (exothermic); IR (ATR, cm⁻¹): ν = 3655 (w), 3579 (w), 3123 (w), 3391 (vw), 3120 (m), 2074 (s), 2048 (vs), 1818 (vw), 1646 (vw), 1522 (m), 1477 (vw), 1425 (w), 1351 (w), 1304 (m), 1290 (m), 1183 (m), 1107 (m), 1067 (w), 1027 (m), 1000 (m), 912 (w), 715 (w), 682 (m), 656 (m), 601 (w), 589 (w), 415 (w)EA (C₈H₂₅Cu₃N₄₂O, 916.22): calcd: C 10.58, H 2.77, N 64.77%; found: C 10.88, H 2.89, N 64.07 %; BAM drop hammer: 15 J; friction tester: > 360 N; ESD: 250 mJ (at grain size < 100 μ m).

[Cu₂(N₃)₄(BTBI)] (**5a**)

After filtration product **5a** was yielded in form of a dark brown solid. Yield: 60.5 mg (0.22 mmol, 87%).

DTA (5 °C min⁻¹) onset: 195 °C (exothermic); IR (ATR, cm⁻¹): ν = 3373 (vw), 3328 (vw), 3111 (m), 2080 (s), 2055 (vs), 2048 (vs), 1670 (vw), 1515 (m), 1499 (m), 1477 (w), 1381 (vw), 1346 (w), 1290 (m), 1269 (m), 1210 (w), 1168 (vw), 1089 (m), 1036 (s), 962 (w), 941 (vw), 871 (m), 838 (w), 692 (w), 658 (w), 616 (s), 605 (m), 594 (m), 584 (m); EA (C₄H₄Cu₂N₁₈, 431.29): calcd: C 11.26, H 0.93, N 58.46%; found: C 11.26, H 1.29, N 57.91%; BAM drop hammer: 2 J; friction tester: < 5 N; ESD: 5 mJ (at grain size < 100 μ m).

[Cu(N₃)(BTBI)] (**5b**)

Single crystals of complex **5b** were received according to the general procedure. An elemental analysis pure isolation of the compound was not possible because of side species formation

[Cu(N₃)₂(AET)] (**6a**)

After stirring for 12 h at room temperature, **6a** was filtered off as brown solid. Yield: 47.5 mg (0.17 mmol, 66%).

DTA (5 °C min⁻¹) onset: 131 °C (exothermic); IR (ATR, cm⁻¹): ν = 3132 (w), 2129 (w), 2097 (s), 2046 (vs), 2007 (m), 1983 (w), 2958 (w), 1512 (w), 1461 (w), 1440 (vw), 1392 (vw), 1339 (w), 1313 (m), 1292 (m), 1267 (m), 1183 (m), 1154 (vw), 1101 (m), 1061 (vw), 1022 (vw), 1002 (w), 945 (w), 902 (M), 789 (vw), 749 (w), 715 (w), 693 (w), 666 (m), 602 (w), 586 (w), 556 (w), 413 (w); EA (C₃H₅CuN₁₃, 286.71): calcd: C 12.57, H 1.76, N 63.51%; found: C 12.27, H 1.74, N 60.28%; BAM drop hammer: < 1 J; friction tester: < 0.1 N; ESD: 1.1 mJ (at grain size < 100 μ m).

$[\text{Cu}_2(\text{N}_3)_4(\text{AET})]$ (**6b**)

Single crystals of compound **6b** were received in a mixture with crystals of complex **6a** according to the general procedure. An elemental analysis pure isolation of the compound was therefore not possible.

$[\text{Cu}(\text{N}_3)_2(\text{APT})]$ (**7**)

Coordination compound **7** was obtained in form of a brown solid after filtration. Yield: 60.5 mg (0.22 mmol, 87%).

DTA ($5\text{ }^\circ\text{C min}^{-1}$) onset: $54\text{ }^\circ\text{C}$ (endothermic), $132\text{ }^\circ\text{C}$ (exothermic); IR (ATR, cm^{-1}): $\nu = 3364$ (vw), 3321 (vw), 3121 (m), 3008 (vw), 2949 (vw), 2884 (vw), 2590 (vw), 2156 (w), 2082 (s), 2047 (vs), 1813 (vw), 1748 (vw), 1505 (m), 1458 (w), 1444 (w), 1436 (w), 1374 (w), 1342 (m), 1321 (w), 1294 (s), 1278 (m), 1243 (m), 1202 (m), 1178 (m), 1149 (w), 1103 (m), 1090 (w), 1039 (m), 1015 (w), 1003 (m), 909 (m), 892 (w), 857 (w), 806 (m), 715 (vw), 692 (w), 681 (m), 659 (m), 648 (m), 628 (m), 602 (w), 586 (w), 555 (w), 466 (vw), 415 (vw), 403 (vw); EA ($\text{C}_4\text{H}_7\text{CuN}_{13}$, 300.74): calcd: C 15.98, H 2.35, N 60.55%; found: C 16.25, H 2.32, N 60.55%; BAM drop hammer: $< 1\text{ J}$; friction tester: 4.5 N ; ESD: 2.5 mJ (at grain size $< 100\text{ }\mu\text{m}$).

$[\text{Cu}_3(\text{N}_3)_6(1\text{-MAT})_2]$ (**8**)

Single crystals of compound **8** were according to the general procedure. Because of side species formation, an elemental analysis pure isolation of the ECC was not possible.

[Cu₄(N₃)₈(2-MAT)₂] (**9**)

Complex **9** was obtained as a brown precipitate. Yield: 164 mg (0.21 mmol, 83%). Suitable crystals in the form of red rods for X-ray diffraction were picked directly out of the reaction mixture.

DTA (5 °C min⁻¹) onset: 161 °C (exothermic); IR (ATR, cm⁻¹): ν = 3415 (m), 3338 (m), 3291 (w), 3245 (w), 3182 (w), 2102 (vs), 2053 (s), 2036 (s), 1634 (s), 1554 (m), 1439 (w), 1425 (m), 1416 (w), 1376 (w), 1352 (w), 1326 (w), 1294 (m), 1266 (m), 1193 (m), 1128 (w), 1105 (w), 1070 (w), 1022 (w), 901 (w), 812 (m), 751 (w), 694 (w), 675 (w), 648 (m); EA (C₄H₁₀Cu₄N₃₆, 788.55) calc.: C 6.09, H 1.28, N 60.39%; found: C 6.67, H 1.58, N 57.57%; BAM drop hammer: < 1 J; friction tester: < 5 N; ESD: 13 mJ (at grain size < 100 μ m).

[Cu₄(N₃)₈(2,2-dte)] (**10**)

Complex **10** precipitated in the form of a dark brown solid. Yield: 121 mg (0.16 mmol, 65%).

DTA (5 °C min⁻¹) onset: 190 °C (exothermic); IR (ATR, cm⁻¹): ν = 3149 (w), 3119 (w), 2252 (vw), 2166 (w), 2112 (vs), 2093 (vs), 2052 (s), 2040 (s), 2032 (s), 2016 (m), 2007 (m), 1997 (w), 1988 (w), 1972 (w), 1958 (w), 1743 (w), 1572 (w), 1467 (w), 1451 (w), 1384 (w), 1340 (m), 1303 (w), 1273 (s), 1273 (s), 1199 (w), 1148 (w), 1137 (m), 1048 (w), 1017 (w), 912 (w), 758 (vw), 720 (m), 693 (m), 682 (w), 655 (w), 586 (w), 577 (m); EA (C₄H₆Cu₄N₃₂, 756.50): calcd: C 6.35, H 0.80, N 59.25%; found: C 6.94, H 1.16, N 56.16%; BAM drop hammer: < 1 J; friction tester: < 5 N; ESD: 5 mJ (at grain size < 100 μ m).

[Cu₂(N₃)₄(1,2-dtp)] (**11**)

Product **11** precipitated as a brown powder out of the mother liquor. Yield: 103 mg (0.22 mmol, 86%).

DTA (5 °C min⁻¹) onset: 146 °C (exothermic); IR (ATR, cm⁻¹): ν = 3151 (w), 3126 (vw), 2088 (s), 2046 (vs), 1572 (vw), 1500 (w), 1466 (vw), 1451 (w), 1439 (w), 1379 (w), 1356 (w), 1339 (w), 1292 (m), 1205 (w), 1183 (w), 1167 (w), 1147 (w), 1103 (w), 1083 (vw), 1054 (vw), 1039 (vw), 1025 (w), 1003 (vw), 983 (m), 908 (w), 899 (w), 872 (vw), 829 (w), 700 (m), 685 (w), 662 (m), 642 (w), 601 (w), 586 (w); EA (C₅H₈Cu₂N₂₀, 475.35): calcd: C 12.63, H 1.70, N 58.93%; found: C 13.14, H 1.85, N 57.93%; BAM drop hammer: 3 J; friction tester: < 5 N; ESD: 18 mJ (at grain size < 100 μ m).

[Cu₄(N₃)₈(2,2-dtp)] (**12**)

Compound **12** was received as a brown solid. Yield: 151 mg (0.20 mmol, 78%).

DTA (5 °C min⁻¹) onset: 195 °C (exothermic); IR (ATR, cm⁻¹): ν = 3143 (w), 2121 (vs), 2096 (vs), 2056 (s), 2044 (m), 2005 (w), 1573 (w), 1465 (w), 1444 (w), 1386 (w), 1349 (w), 1304 (w), 1278 (m), 1201 (w), 1167 (w), 1158 (vw), 1141 (w), 1083 (vw), 1053 (w), 1017 (w), 962 (w), 910 (w), 848 (w), 758 (vw), 694 (m), 680 (w), 650 (w), 589 (w), 577 (w); EA (C₃H₁₀Cu₄N₃₂, 770.53): calcd: C 7.79, H 1.05, N 58.17%; found: C 7.98, H 1.27, N 54.18%; BAM drop hammer: 1 J; friction tester: < 5 N; ESD: 5 mJ (at grain size < 100 μ m).

[Cu₂(N₃)₄(i-dtp)] (**13**)

Azide complex **13** was isolated as a brown precipitate. Yield: 84.8 mg (0.18 mmol, 71%).

DTA (5 °C min⁻¹) onset: 165 °C (exothermic); IR (ATR, cm⁻¹): ν = 3362 (vw), 3318 (vw), 3100 (w), 3012 (vw), 2976 (vw), 2089 (s), 2072 (s), 2041 (vs), 1825 (vw), 1498 (w), 1464 (w), 1444 (w), 1397 (w), 1372 (vw), 1345 (w), 1281 (m), 1202 (w), 1182 (m), 1124 (w), 1107 (w), 1091 (m), 1054 (vw), 1041 (w), 1005 (m), 911 (w), 792 (vw), 715 (vw), 681 (m), 666 (m), 602 (w), 589 (w); EA

(C₅H₈Cu₂N₂₀, 475.35): calcd: C 12.63, H 1.70, N 58.93%; found: C 13.14, H 1.80, N 57.90%; BAM drop hammer: 2 J; friction tester: < 5 N; ESD: 5 mJ (at grain size < 100 μm).

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