Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

2-Methylsubstituted monotetrazoles in copper(II) perchlorate complexes: manipulating coordination chemistry and derived energetic properties

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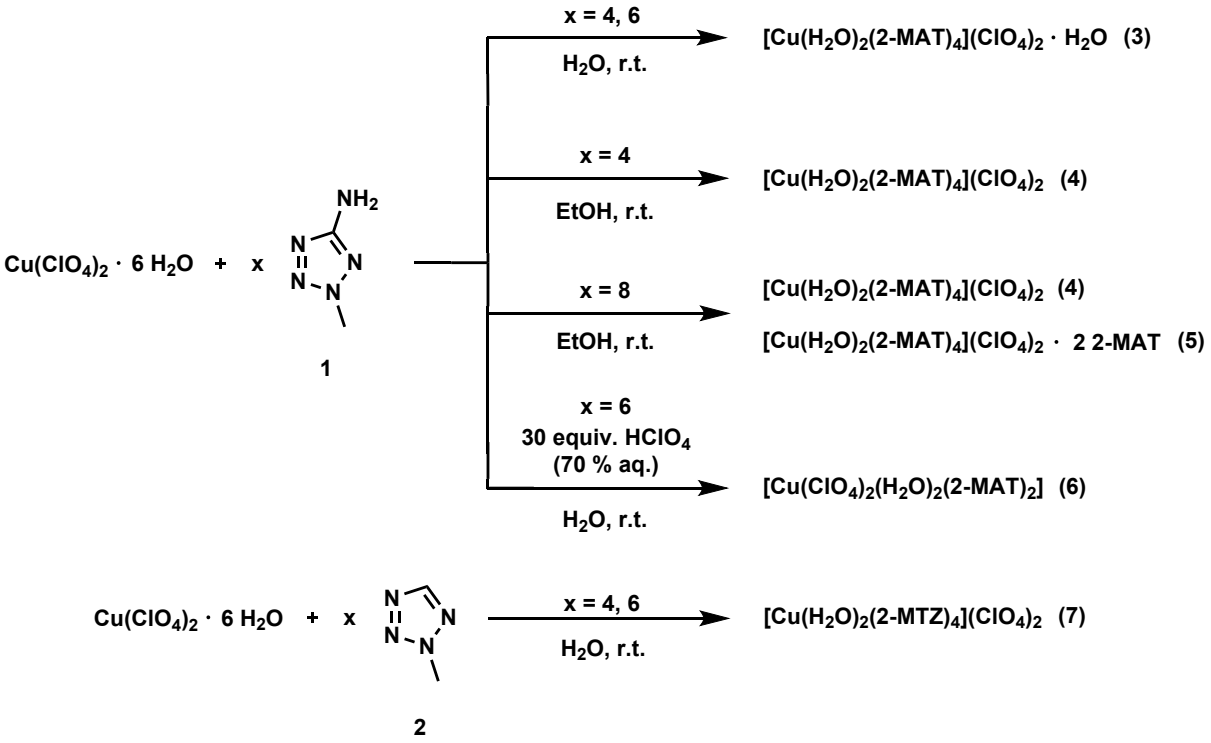
1. Overview of synthesized compounds



2. Experimental and general methods

All chemicals and solvents were employed as received (Sigma-Aldrich, Fluka, Acros, ABCR). ^{1}H and ^{13}C spectra were recorded at ambient temperature using a JEOL Bruker 400, Eclipse 270, JEOL EX 400 or a JEOL Eclipse 400 instrument. The chemical shifts quoted in ppm in the text refer to typical standards such as tetramethylsilane (^{1}H, ^{13}C) in d_6-DMSO as the solvent. Endothermic and exothermic events of the described compounds, which indicate melting, evaporation 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 instrument and partly by differential scanning calorimetry (DSC) with a LINSEIS DSC PT10 and partly by thermal gravimetric analysis (TGA) with a PerkinElmer TGA4000. Differential thermal analysis measurements were carried out in open glass tubes with approximately 3–4 mg substance, TGA measurements with 1-2 mg substance in total in Al_2O_3 crucibles, whereas the differential scanning calorimetric measurements were performed with about 1 mg substance in a perforated aluminium vessel and a nitrogen flow of 5 dm^3 h^{-1}. Both devices were calibrated with the literature known melting point of Indium. The balance of the TGA device was calibrated with a 55.97 mg ball and the temperature calibrated with the Perkin Elmer calibration kit including three different metals or alloys (alumel, nickel, perkalloy, iron). Infrared spectra were measured with pure 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 those calculated due to their explosive behaviour). UV-Vis spectra were recorded in the solid state using a Varian Cary 500 spectrometer in the wavelength range of 350–1000 nm. Impact sensitivity tests were carried out according to STANAG 4489[S1] with a modified instruction[S2] using a BAM (Bundesanstalt für Materialforschung) drophammer.[S3, S4] Friction sensitivity tests were carried out according to STANAG 4487[S5] with a modified instruction[S6] using the BAM friction tester. The classification of the tested compounds results from the "UN Recommendations on the Transport of Dangerous Goods".[S7] Additionally, all compounds were tested to determine the sensitivity toward electrical discharge using the OZM Electric Spark Tester ESD 2010 EN or OZM Electric Spark XSpark10 device.[S3] Hot plate and hot needle tests were performed in order to classify the 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 behaviour 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 fibre with a core diameter of 400 µm and a cladding diameter of 480 µm. The optical fibre is connected via a SMA type connecter 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 complex 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 A, and pulse length of 0.1 ms. The combined current and pulse length result in an energy output of about 0.17 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 potentially explosive energetic materials, which show partly increased sensitivities towards 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. Especially the very sensitive compound* ***6***

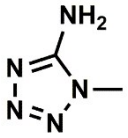
must be handled with great care! Whenever handling concentrated perchloric acid, avoid combining it with organic solvents due to the explosive potential of the resulting mixtures.

Dimethyl sulfate is carcinogenic, mutagenic, highly poisonous, corrosive, environmentally hazardous. In addition to the standard safety instructions, it is recommended to wear gloves with this toxic chemical at all times.

Methylation of 5-aminotetrazole

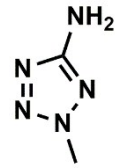
The synthesis of the methylated species **1** and **2** was performed to a slightly modified literature procedure from Ismael *et al.*.[S8] At first, 5-aminotetrazole (11.9 g, 140 mmol, 1.0 equiv.) was suspended in water (30 mL) and an aqueous solution of sodium hydroxide (20 wt. %, 100 mL) was added to the suspension until complete dissolution of the starting material. The subsequent, dropwise addition of dimethylsulfate (26.9 mL, 148 mmol, 1.1 equiv.) was accompanied by sequentially maintaining the reaction alkaline (20 wt % NaOH, phenolphthalein as indicator). After complete addition of dimethylsulfate, the obtained mixture was refluxed for 1 hour and cooled to 3 °C. After two days, the product could be filtrated and recrystallized from water yielding colourless crystals of 1-methyl-5-aminotetrazole (**1**, 5.69 g, 57.4 mmol, 41 %). The collected filtrate was repeatedly extracted with diethylether, the combined organic phases were dried, and the solvent was evaporated *in vacuo*. The hereby obtained colourless residue was recrystallized from water yielding 2-methyl-5-aminotetrazole (**2**) as colourless crystals (4.02 g, 47.8 mmol, 34 %). Conducted characterization for **1** and **2** was consistent with data provided by Cristiano and coworkers.[S8]

1-Methyl-5-aminotetrazole



^{1}H NMR (DMSO-d_6, 25 °C, ppm): δ = 3.70 (s, 3H, -CH_3), 6.64 (s, 2H, -NH_2); **^{13}C NMR** (DMSO-d_6, 25 °C, ppm): δ = 32.0 -CH_3), 156.3 (CN$_4$); **DSC** (5 °C min^{-1}) onset: 225 °C (endothermic); **IR** (ATR, cm^{-1}): $\tilde{\upsilon}$ = 3314 (s), 3148 (vs), 2951 (w), 1667 (vs), 1594 (vs), 1486 (s), 1462 (m), 1320 (s), 1279 (m), 1236 (m), 1162 (w), 1120 (m), 1087 (s), 1045 (s), 969 (m), 863 (w), 789 (m), 742 (m), 672 (vs), 632 (s), 624 (s); **EA**: ($C_2H_5N_5$, 99.10) calc.: C 24.24, H 5.09, N 70.67 %; found: C 24.11, H 4.96, N 66.22 %; **BAM drophammer**: > 40 J; **friction tester**: > 360 N; **ESD**: 1.50 J (at grain size 500–1000 µm).

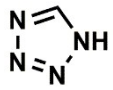
2-Methyl-5-aminotetrazole (1)



^{1}H NMR (DMSO-d_6, 25 °C, ppm): δ = 4.08 (s, 3H, -CH_3), 5.96 (s, 2H, -NH_2); **^{13}C NMR** (DMSO-d_6, 25 °C, ppm): δ = 167.6 (CN$_4$); **DTA** (5 °C min^{-1}) onset: 104 °C (endothermic), 252 °C (endothermic); **TGA** (5 °C min^{-1}): 110–200 °C (melting and evaporation of 2-MAT), 210–400 °C (further evaporation of 2-MAT) **IR** (ATR, cm^{-1}): $\tilde{\upsilon}$ = 3374 (s, N-H), 3304 (s, N-H), 3216 (m, N-H), 3086 (w, C-H), 1628 (s), 1549 (vs, C=N), 1446 (m), 1420 (m), 1409 (s), 1377 (m), 1340 (w), 1314 (m), 1203 (s), 1150 (w), 1122 (w), 1084 (w), 1054 (m), 1015 (m), 959 (w), 901 (w), 808 (m), 756 (s), 740 (w), 712 (w), 689 (w), 678 (w), 647 (vs),

606 (s); **EA**: ($C_2H_5N_5$, 99.10) calc.: C 24.24, H 5.09, N 70.67 %; found: C 24.40, H 4.99, N 70.75 %; **BAM drophammer**: > 40 J; **friction tester**: > 360 N; **ESD**: 1.50 J (at grain size 100–500 µm).

1,5*H*-Tetrazole



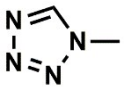
According to a modified procedure from Thomann *et al.*,[S9] sodium azide (39.0 g, 600 mmol, 1.0 equiv.) and ammonium chloride (31.8 g, 600 mmol, 1.0 equiv.) were suspended in triethyl orthoformate (266 g, 1.80 mol, 3.0 equiv.). In the following, glacial acetic acid (144 g, 2.40 mol, 4.0 equiv.) was added drop wise and the resulting mixture was refluxed for ten hours at 80 °C. Afterwards, the suspension was evaporated to dryness, acetone (600 mL) was added and the obtained mixture was heated and filtrated while hot. The filtrate was evaporated to dryness again and the residue was recrystallized from ethyl acetate yielding 1,5*H*-tetrazole as light orange crystals (13.3 g, 190 mmol, 32 %). The filtrate was evaporated to dryness and recrystallized again from ethyl acetate giving another batch of 1,5*H*-tetrazole (8.20 g, 117 mmol, 20 %). Analytical data are consistent with previously reported results.[S9]

^{1}H NMR (DMSO-d_6, 25 °C, ppm): δ = 9.38 (s, 1H, -C*H*); **^{13}C NMR** (DMSO-d_6, 25 °C, ppm): δ = 143.6 (*C*N_4). **DSC** (5 °C min^{-1}) onset: 104 °C (endothermic); **IR** (ATR, cm^{-1}): $\tilde{\upsilon}$ = 3374 (s), 3304 (s), 3216 (m), 3086 (w), 1628 (s), 1549 (vs), 1446 (m), 1420 (m), 1409 (s), 1377 (m), 1340 (w), 1314 (m), 1203 (s), 1150 (w), 1122 (w), 1084 (w), 1054 (m), 1015 (m), 959 (w), 901 (w), 808 (m), 756 (s), 740 (w), 712 (w), 689 (w), 678 (w), 647 (vs), 606 (s).

Methylation of 1,5*H*-tetrazole

According to a literature procedure from Gaponik *et al.*,[S10] a stirring suspension of 1,5*H*-tetrazole (8.00 g, 114 mmol, 1.0 equiv.) and K_2CO_3 (15.9 g, 115 mmol, 1.0 equiv.) in acetone (30 mL) was charged with methyl iodide (8.0 mL, 129 mmol, 1.1 equiv.) in a dropwise manner. After keeping the resulting reaction mixture under reflux for 16 h, cooling to room temperature was followed by filtration and several washings of the obtained residue with acetone. Concentration of the filtrate and subsequent vacuum distillation of the resulting crude product gave 2-methyl-5*H*-tetrazole (**1**, 40 °C, 12 mbar, 2.22 g, 26.6 mmol, 23 %) as a colourless liquid and 1-methyl-5*H*-tetrazole (90 °C, 0.01 mbar, 4.59 g, 54.6 mmol, 48 %) as colourless crystals.

1-Methyl-5*H*-tetrazole



^{1}H NMR (DMSO-d_6, 25 °C, ppm) δ: 9.31 (s, 1H, -C*H*), 4.10 (s, 3H, -CH_3); **^{13}C NMR** (DMSO-d_6, 25 °C, ppm) δ: 144.5 (-*C*N_4), 34.1 (-*C*H_3); **DTA** (5 °C min^{-1}): 39 °C (endothermic), 206 °C (exothermic); **IR** (ATR, cm^{-1}): $\tilde{\upsilon}$ = 3111 (m), 3032 (vw), 2962 (vw), 1843 (vw), 1491 (m), 1477 (m), 1471 (m), 1445 (w), 1422 (w), 1413 (w), 1384 (vw), 1276 (w), 1220 (w), 1172 (s), 1107 (vs), 1053 (w), 1043 (w), 1019 (w), 965 (s), 924 (m), 876 (w), 722 (w), 678 (vs), 664 (s), 657 (s); **EA**: ($C_2H_4N_4$, 84.08) calc.: C 28.57, H 4.80, N 66.63 %; found: C 28.47, H 4.89, 37 N 65.51 %; **BAM drophammer**: > 40 J; **friction tester**: > 360 N; **ESD**: 1.50 J (at grain size < 100 µm).

2-Methyl-5*H*-tetrazole (2)

^{1}H NMR (DMSO-d_6, 25 °C, ppm) δ: 8.92 (s, 1H, -C*H*), 4.38 (s, 3H, -CH_3); **^{13}C NMR** (DMSO-d_6, 25 °C, ppm) δ: 153.2 (-CN_4), 39.3 (-CH_3); **DTA** (5 °C min^{-1}): 152 °C (endothermic); **TGA** (5 °C min^{-1}): 30–100 °C (evaporation of 2-MTZ due to high vapor pressure), 152 °C (boiling point of 2-MTZ); **IR** (ATR, cm^{-1}): $\tilde{\upsilon}$ = 3142 (vw, C-H), 2964 (vw, C-H), 2215 (vw), 1767 (vw), 1717 (vw), 1630 (vw), 1443 (m, C=N), 1411 (w), 1362 (m), 1278 (s), 1178 (m), 1137 (m), 1039 (s), 1017 (m), 885 (m), 708 (s), 699 (vs), 681 (vs), 665 (w), 484 (w), 476 (w), 466 (w), 434 (w), 434 (w), 427 (w), 419 (w); **EA**: ($C_2H_4N_4$, 84.08) calc.: C 28.57, H 4.80, N 66.63 %; found: C 28.49, H 4.65, N 66.17 %; **BAM drophammer**: > 40 J; **friction tester**: > 360 N; **ESD**: 1.50 J (at grain size 100–500 µm).

$[Cu(H_2O)_2(2\text{-}MAT)_4](ClO_4)_2 \cdot H_2O$ (3)

To a mechanically stirred aqueous solution (1 mL) of $Cu(ClO_4)_2 \cdot 6\,H_2O$ (92.6 mg, 0.25 mmol, 1.0 equiv.), 2-methyl-5-aminotetrazole (**1**, 99.1 mg, 1.00 mmol, 4.0 equiv.) dissolved in water (2 mL) was added dropwise. In the course of crystallization and purification, and within four days, **3** could be isolated in the form of blue blocks suitable for X-ray diffraction (90.4 mg, 0.13 mmol, 52 %).

DTA (5 °C min^{-1}) onset: 125 °C (endothermic), 176 °C (exothermic); **IR** (ATR, cm^{-1}): $\tilde{\upsilon}$ = 3447 (m, O-H/N-H), 3340 (m, O-H/N-H), 1632 (s, C=N), 1552 (m), 1442 (m), 1420 (w), 1385 (w), 1349 (w), 1331 (w), 1193 (w), 1064 (vs, Cl-O), 936 (w), 811 (m), 750 (m), 674 (w), 649 (m), 623 (s); **EA**: ($C_8H_{26}Cl_2CuN_{20}O_{11}$, 712.87) calc.: C 13.48, H 3.68, N 39.30 %; found: C 13.43, H 3.58, N 39.32 %; BAM drophammer: 5 J; **friction tester**: 30 N; **ESD**: 0.26 J (at grain size 500–1000 µm).

$[Cu(H_2O)_2(2\text{-}MAT)_4](ClO_4)_2$ (4) & $[Cu(H_2O)_2(2\text{-}MAT)_4](ClO_4)_2 \cdot 2$ 2-MAT (5)

The ligand 2-methyl-5-aminotetrazole (**1**, 198 mg, 2.00 mmol, 8.0 equiv.) was dissolved in ethanol (2 mL) and slowly added to an ethanolic solution (1 mL) of the used copper(II) species $Cu(ClO_4)_2 \cdot 6\,H_2O$ (92.6 mg, 0.25 mmol, 1.0 equiv.). The resulting reaction mixture soon began to mist leading to a turquoise precipitate which was filtered immediately. After six days, compound **4** crystallized from the filtrate in the form of blue blocks suitable for X-ray diffraction (82.8 mg, 0.12 mmol, 48 %). The residue of the previous filtration contained a mixture of **4** and the light green compound **5**. The structure of the latter has been determined through X-ray diffraction. To avoid the precipitation of **5**, the perchlorate complex **4** can also be isolated through an analogous synthesis using only four equivalents of 2-MAT.

$[Cu(H_2O)_2(2\text{-}MAT)_4](ClO_4)_2$ (4)

DTA (5 °C min^{-1}) onset: 110 °C (endothermic), 171 °C (exothermic); **IR** (ATR, cm^{-1}): $\tilde{\upsilon}$ = 3487 (m, O-H/N-H), 3426 (m, O-H/N-H), 3385 (m, O-H/N-H), 3347 (m, O-H/N-H), 3244 (w, O-H/N-H), 1634 (s, C=N), 1555 (s), 1439 (m), 1386 (w), 1351 (w), 1335 (w), 1210 (w), 1191 (w), 1143 (m), 1117 (s), 1101 (s), 1033 (s, Cl-O), 925 (m), 815 (m), 769 (m), 756 (m), 747 (m), 724 (m), 674 (m), 666 (m), 643 (s), 623 (vs); **EA**: ($C_8H_{26}Cl_2CuN_{20}O_{11}$, 694.86) calc.: C 13.83, H 3.48, N 40.32 %; found: C 14.10, H 3.48, N 40.08 %; **BAM drophammer**: < 1 J; **friction tester**: 24 N; **ESD**: 20 mJ (at grain size < 100 µm).

$[Cu(ClO_4)_2(H_2O)_2(2\text{-MAT})_2]$ (6)

A solution of 2-methyl-5-aminotetrazole (**1**, 99.1 mg, 1.00 mmol, 4.0 equiv.) in water (2 mL) was slowly added to an aqueous solution (1 mL) of $Cu(ClO_4)_2 \cdot 6\,H_2O$ (92.6 mg, 0.25 mmol, 1.0 equiv.). Before stirring mechanically for 10 min, $HClO_4$ (70 % wt., 0.5 mL, 8.3 mmol, 30 equiv.) was added. The copper(II) perchlorate complex **6** with coordinating perchlorate anions was obtained after four days in the form of blue rods suitable for X-ray diffraction (93.7 mg, 0.19 mmol, 76 %).

DTA (5 °C min^{-1}) onset: 192 °C (exothermic); **TGA** (5 °C min^{-1}): 195 °C (dec.); **IR** (ATR, cm^{-1}): $\tilde{\upsilon}$ = 3450 (m, O-H/N-H), 3361 (m, O-H/N-H), 1634 (s, C=N), 1563 (m), 1428 (w), 1382 (w), 1334 (w), 1192 (w), 1048 (vs, Cl-O), 937 (m), 811 (m), 748 (m), 691 (m), 673 (m), 648 (m), 621 (vs); **EA**: ($C_4H_{14}Cl_2CuN_{10}O_{10}$, 496.66) calc.: C 9.67, H 2.84, N 28.20 %; found: C 9.78, H 2.96, N 27.50 %; **BAM drophammer**: 2 J; **friction tester**: 2.2 N; **ESD**: 0.15 J (at grain size < 100 µm).

$[Cu(H_2O)_2(2\text{-MTZ})_4](ClO_4)_2$ (7)

2-Methyltetrazole (**2**, 84.1 mg, 1.25 mmol, 4.0 equiv.) was added to a stirred aqueous solution (1 mL) of copper(II) perchlorate hexahydrate (92.6 mg, 0.25 mmol, 1.0 equiv.). Resulting from subsequent crystallization at room temperature, $[Cu(H_2O)_2(2\text{-MTZ})_4](ClO_4)_2$ (**7**, 114.3 mg, 0.18 mmol, 73 %) was obtained within a day as blue blocks, suitable for X-ray determination.

DTA (5 °C min^{-1}): 115 °C (endothermic), 208 °C (endothermic), 240 °C (exothermic);); **TGA** (5 °C min^{-1}): 75–110 °C (loss of coordinating aqua ligands), 140–208 °C (partial loss of 2-MTZ ligands), 240 °C (dec.); **IR** (ATR, cm^{-1}): $\tilde{\upsilon}$ = 3522 (m, O-H/N-H), 3475 (m, O-H/N-H), 3160 (w, C-H), 3147 (w, C-H), 1634 (w, C=N), 1473 (vw), 1447 (w), 1428 (w), 1369 (w), 1314 (w), 1297 (m), 1196 (w), 1155 (m), 1070 (vs, Cl-O), 1041 (s), 1020 (s), 935 (w), 898 (m), 704 (s), 684 (s), 623 (s); **EA**: ($C_8H_{20}Cl_2CuN_{16}O_{10}$, 634.80): calc.: C 15.14, H 3.18, N 35.30 %; found: C 15.39, H 3.05, N 34.97 %; **BAM drophammer**: 5 J; **friction tester**: 5 N; **ESD**: 50 mJ (at grain size 100–500 µm).

3. IR spectroscopy of 1–7

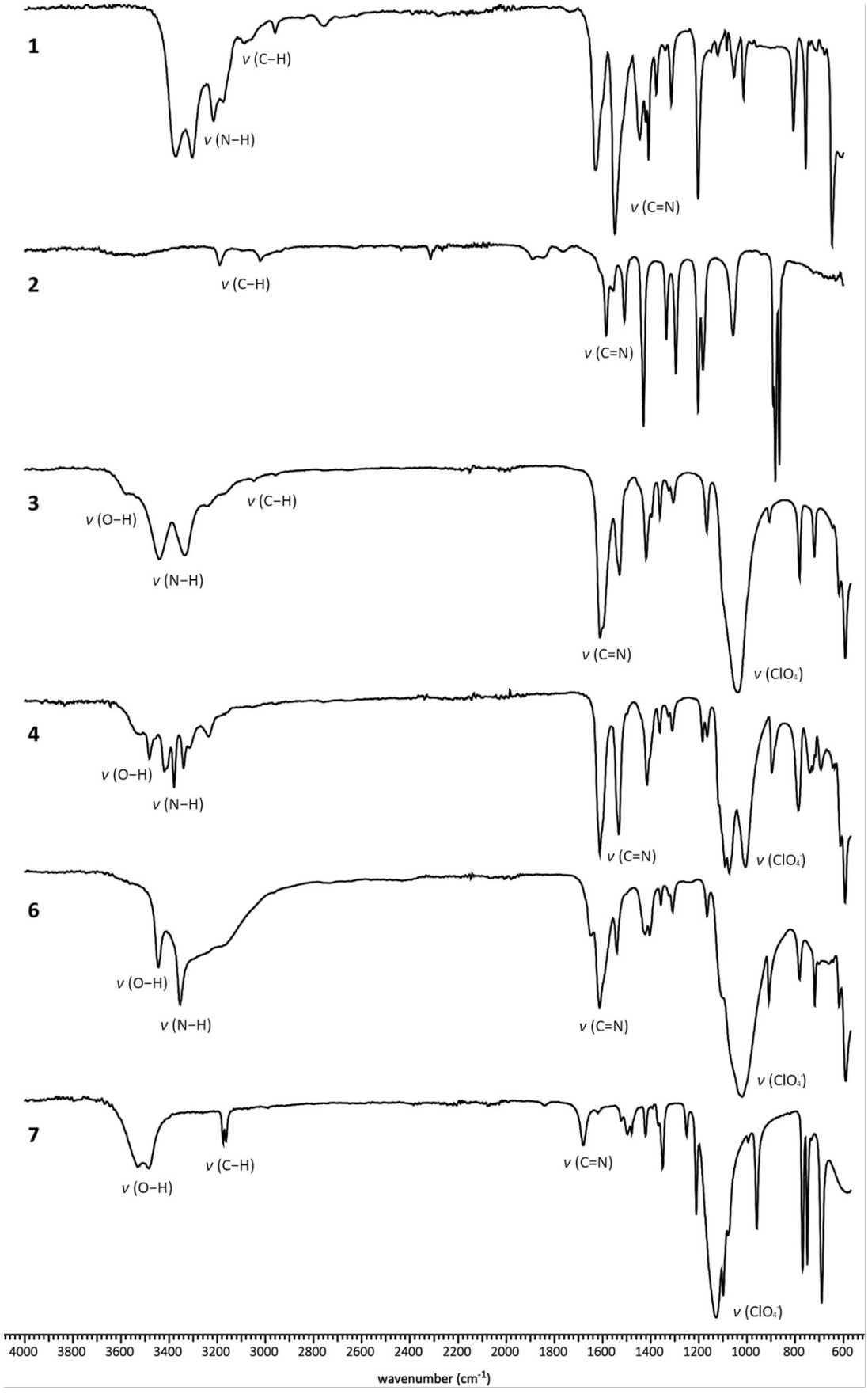


Figure S1 IR spectra of the ligand **1** and **2** as well as the ECC **3**, **4**, **6**, and **7**.

4. 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 (λ = 0.7107 Å). On the Oxford device, data collection and reduction were carried out using the CRYSALISPRO software[S11]. 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[S12], SIR-97[S13], or SHELXS-97[S14]) and refined by full-matrix least-squares on *F*2 (SHELXL[S14]) and finally checked using the PLATON software[S15] integrated in the WinGX[S16] 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 multiscan method[S17, S18]. All DIAMOND2 plots are shown with thermal ellipsoids at the 50 % probability level and hydrogen atoms are shown as small spheres of arbitrary radius.

$[Cu(H_2O)_2(2\text{-}MTZ)_4](ClO_4)_2$ (7)

By examining received data along the crystallographic *c*-axis, the three-dimensional topology of **7**, which is built up by a layer structure comprising of $[Cu(H_2O)_2(2\text{-}MTZ)_4](ClO_4)_2$ units with altering alignment along *b* becomes clear (Figure 8). In between the observed complex-formed pattern, perchlorate counter-anions once again act as the layers' "cohesive" due to the provision of several hydrogen bond acceptors for aqua and tetrazole ligands.

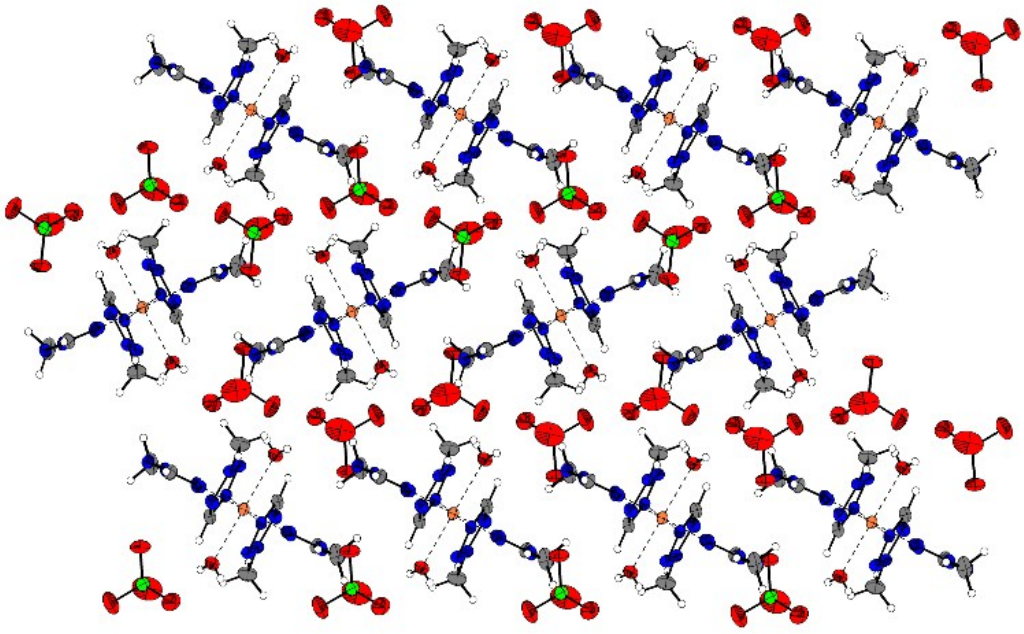


Figure S2 Structure of **7** with the direction of view along the crystallographic *c*-axis.

Table S1 Crystallographic data of **3–5**.

	3	**4**	**5**
Formula	$C_8H_{26}Cl_2CuN_{20}O_{11}$	$C_8H_{24}Cl_2CuN_{20}O_{10}$	$C_{10}H_{29}Cl_2CuN_{25}O_{10}$
FW [g mol^{-1}]	712.93	694.91	794.02
Crystal system	Monoclinic	Monoclinic	Triclinic
Space Group	*C*2/*c*	$P2_1$	*P*–1
Color / Habit	Blue blocks	Blue blocks	Blue blocks
Size [mm]	0.15 x 0.15 x 0.20	0.16 x 0.35 x 0.59	0.11 x 0.28 x 0.42
a [Å]	37.8504(12)	7.8894(7)	10.6159(6)
b [Å]	18.5558(5)	19.9150(15)	10.7796(5)
c [Å]	18.0159(5)	8.3691(6)	13.8295(7)
α [°]	90	90	89.498(4)
β [°]	116.272(3)	101.004(8)	80.568(4)
γ [°]	90	90	83.990(4)
V [Å^3]	11346.3(6)	1290.76(18)	1552.55(14)
Z	16	2	2
$\rho_{calc.}$ [g cm^{-3}]	1.669	1.788	1.699
μ [mm^{-1}]	1.043	1.140	0.964
F(000)	5840	710	814
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173	173	173
θ Min–Max [°]	4.1, 26.0	4.4, 28.0	4.2, 26.0
Dataset	−46:46; −22:22; −22:22	−10:10; −18:26; −11:11	–13:13; –13:12; –14:17
Reflections collected	46903	11360	11962
Independent refl.	11093	4524	6072
R_{int}	0.082	0.041	0.032
Observed reflections	7133	3937	4695
Parameters	815	423	494
R_1 (obs)[a]	0.0644	0.0511	0.0386
wR_2 (all data)[b]	0.1680	0.1278	0.0976
GooF[c]	1.05	1.05	1.03
Resd. Dens. [e Å^{-3}]	−0.50, 1.24	–0.37, 3.24	–0.29, 0.46
Absorption correction	multi-scan	multi-scan	multi-scan
CCDC	1850124	1850121	1850122

a) $R_1 = \Sigma||F_0|- |F_c||/ \Sigma|F_0|$; b) $wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0)^2]]^{1/2}$; $w = [\sigma c^2(F_0^2)+(xP)^2+yP]^{-1}$ and $P=(F_0^2+2F_c^2)/3$; c) GooF = $\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$ (n = number of reflections; p = total number of parameters).

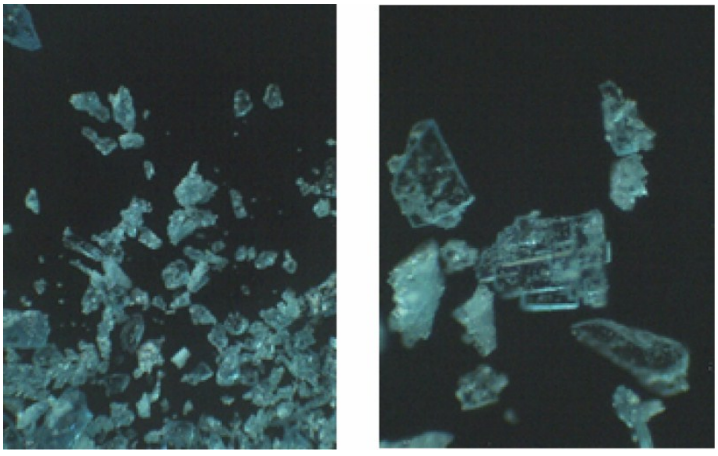


Figure S3 Microscope image of **3** (left; fourfold magnitude) and **4** (right; tenfold magnitude).

Table S2 Crystallographic data of **6** and **7**.

	6	**7**
Formula	$C_4H_{14}Cl_2CuN_{10}O_{10}$	$C_8H_{20}Cl_2CuN_{16}O_{10}$
FW [g mol^{-1}]	496.69	634.80
Crystal system	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$P2_1$
Color / Habit	Blue rods	Blue blocks
Size [mm]	0.10 x 0.14 x 0.22	0.08 x 0.21 x 0.31
a [Å]	7.0476(3)	7.9548(3)
b [Å]	7.4569(3)	14.4157(6)
c [Å]	15.8059(6)	10.8494(4)
α [°]	90	90
β [°]	96.021(4)	95.303(3)
γ [°]	90	90
V [Å^3]	826.07(6)	1238.82(8)
Z	2	2
$\rho_{calc.}$ [g cm^{-3}]	1.997	1.702
μ [mm^{-1}]	1.722	1.175
F(000)	502	646
$\lambda_{MoK\alpha}$ [Å]	0.71069	0.71073
T [K]	173	173
θ Min–Max [°]	4.3, 26.0	4.4, 26.0
Dataset	−8:8; −9:9; −18:19	–9: 9 ; –14:17 ; –12:13
Reflections collected	6210	9189
Independent refl.	1617	2417
R_{int}	0.023	0.040
Observed reflections	1480	1935
Parameters	160	187
R_1 (obs)[a]	0.0369	0.0412
wR_2 (all data)[b]	0.1030	0.1093
GooF[c]	1.07	1.05
Resd. Dens. [e Å^{-3}]	–0.54, 0.78	–0.50, 0.79
Absorption correction	multi-scan	multi-scan
CCDC	1850120	1850123

a) $R_1 = \Sigma||F_0|- |F_c||/ \Sigma|F_0|$; b) $wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0)^2]]^{1/2}$; $w = [\sigma c^2(F_0^2)+(xP)^2+yP]^{-1}$ and $P=(F_0^2+2F_c^2)/3$; c) GooF = $\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$ (n = number of reflections; p = total number of parameters).

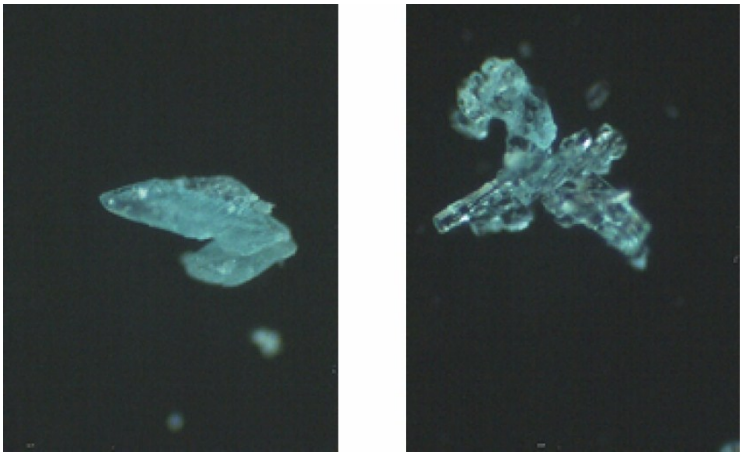


Figure S4 Microscope image of **6** (left; fourfold magnitude) and **7** (right; tenfold magnitude).

5. DTA plots of 1–7

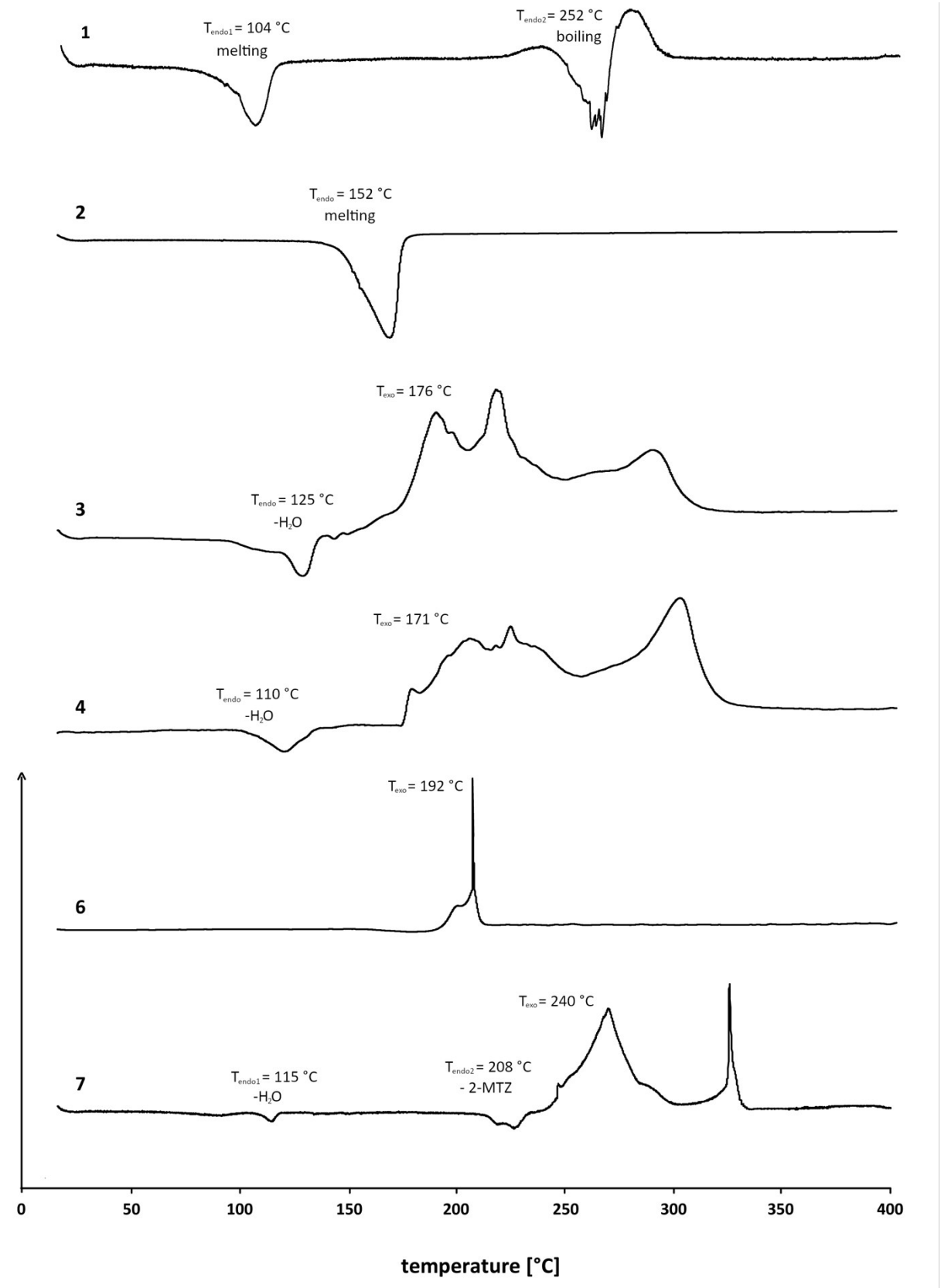


Figure S5 DTA plots of **1**–**4**, **6**, and **7**.

6. TGA plots of 1-4

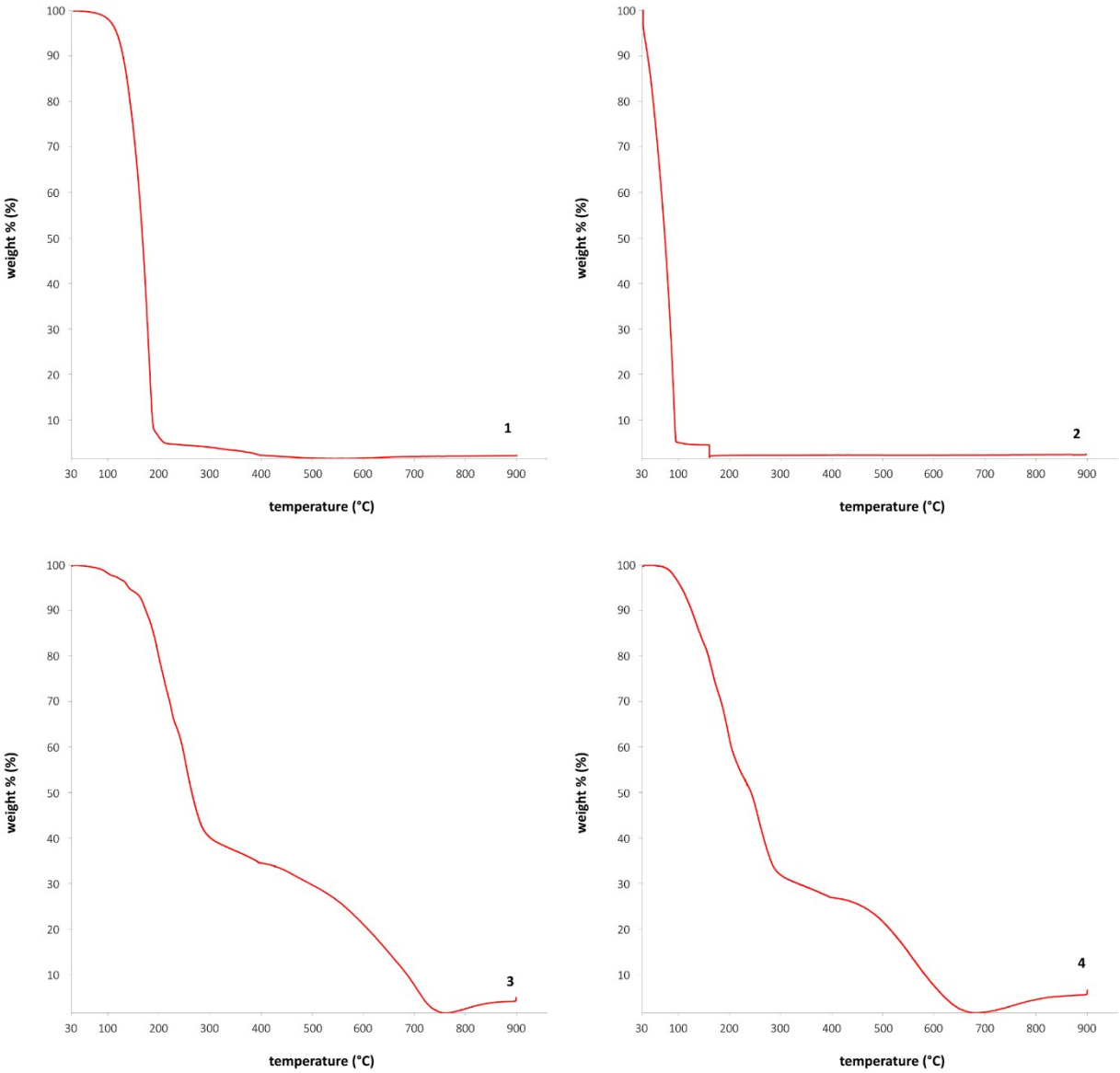


Figure S6 TGA plots (5 °C min^{-1}) of the ligands **1** and **2** as well as the copper(II) perchlorate complexes **3** and **4**.

7. Hot plate, Hot needle and optical initiation tests

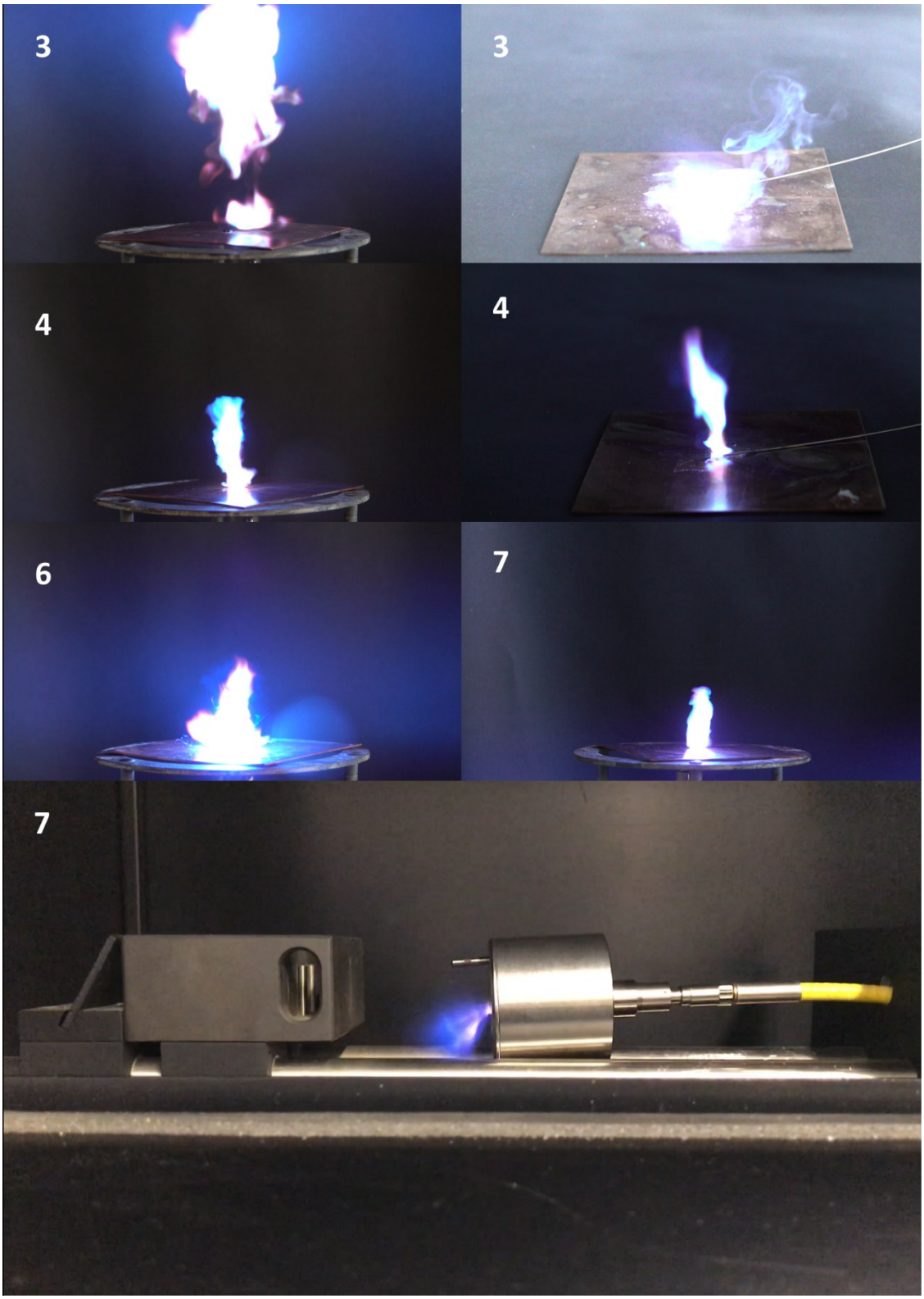


Figure S7 Hot plate tests of **3**, **4**, **6** and **7**, hot needle tests of **3** and **4**, as well as optical initiation of **7**.

8. References

(S1) NATO standardization agreement (STANAG) on explosives, impact sensitivity tests, no. 4489, 1st ed., Sept. 17, **1999**.

(S2) WIWEB-Standardarbeitsanweisung 4-5.1.02, Ermittlung der Explosionsgefährlichkeit, hier der Schlagempfindlichkeit mit dem Fallhammer, Nov. 8, **2002**.

(S3) http://www.ozm.cz, Accessed May 2018.

(S4) http://www.bam.de, Accessed May 2018.

(S5) NATO standardization agreement (STANAG) on explosive, friction sensitivity tests, no. 4487, 1st ed., Aug. 22, **2002**.

(S6) WIWEB-Standardarbeitsanweisung 4-5.1.03, Ermittlung der Explosionsgefährlichkeit oder der Reibeempfindlichkeit mit dem Reibeapparat, Nov. 8, **2002**.

(S7) Impact: insensitive > 40 J, less sensitive ≥ 35 J, sensitive ≥ 4 J, very sensitive ≤ 3 J; Friction: insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N and > 80 N, very sensitive ≤ 80 N, extremely sensitive ≤ 10 N. According to the UN Recommendations on the Transport of Dangerous Goods, (+) indicates not safe for transport.

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(S15) A. L. Spek, *PLATON*, *A Multipurpose Crystallographic Tool*, Utrecht University, The Netherlands, **1999**.

(S16) L. J. Farrugia, *J. Appl. Cryst.*, 2012, **45**, 849–854.

(S17) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm (CrysAlisPro Oxford Diffraction Ltd., Version 171.33.41, **2009**).

(S18) *APEX3*. Bruker AXS Inc., Madison, Wisconsin, USA.