Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

Highly functional energetic complexes: stability tuning through coordination diversity of isomeric propyl-linked ditetrazoles

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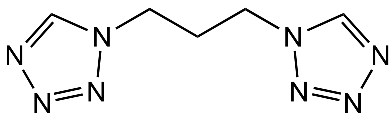
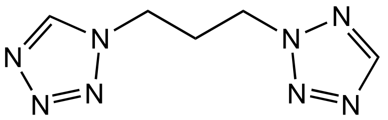
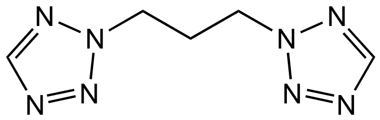
1. Compounds overview



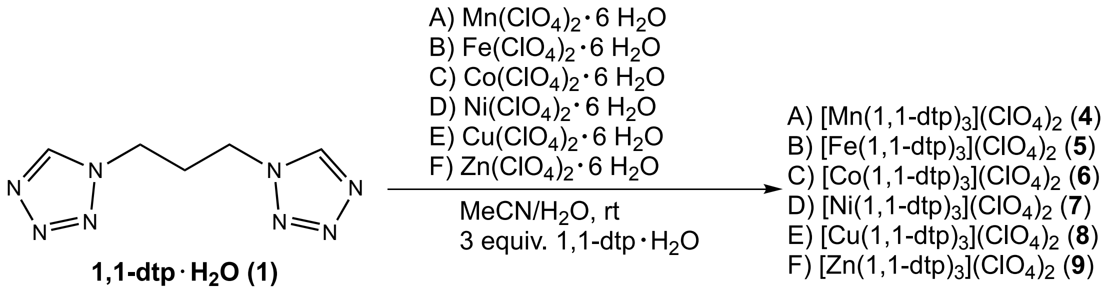
1,1-dtp ·H$_2$O (1)

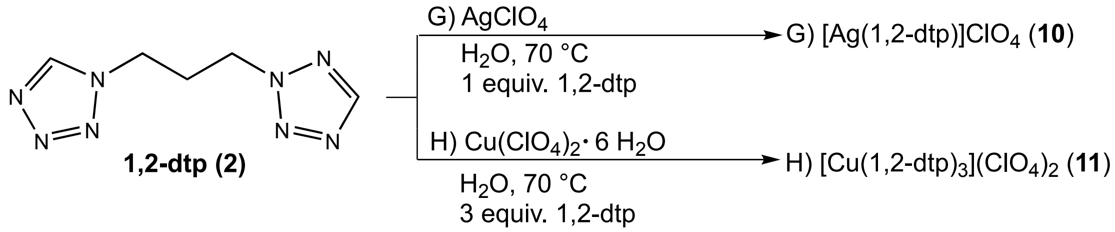


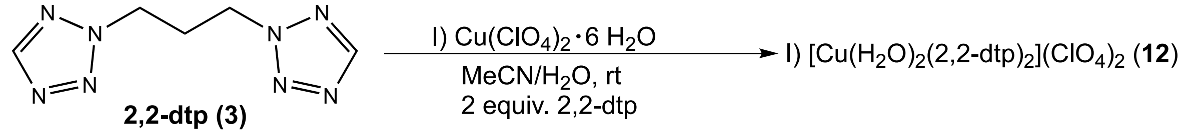
1,2-dtp (2)

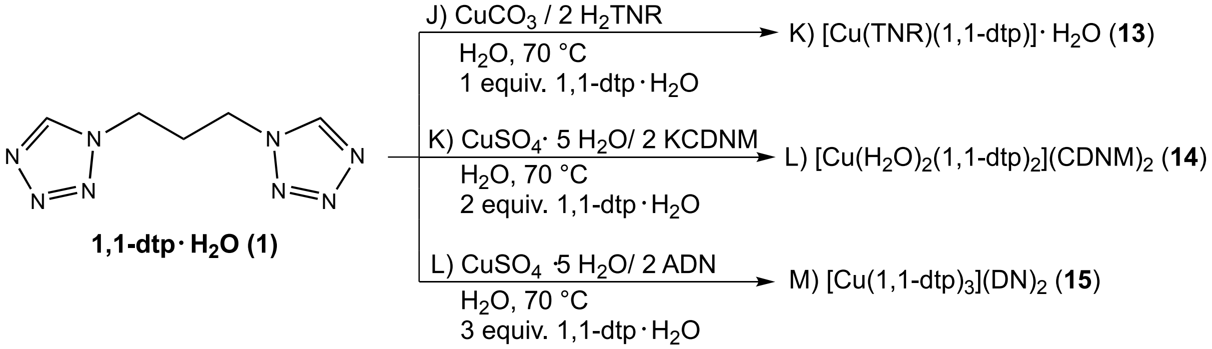


2,2-dtp (3)









2. IR spectroscopy of 1–15

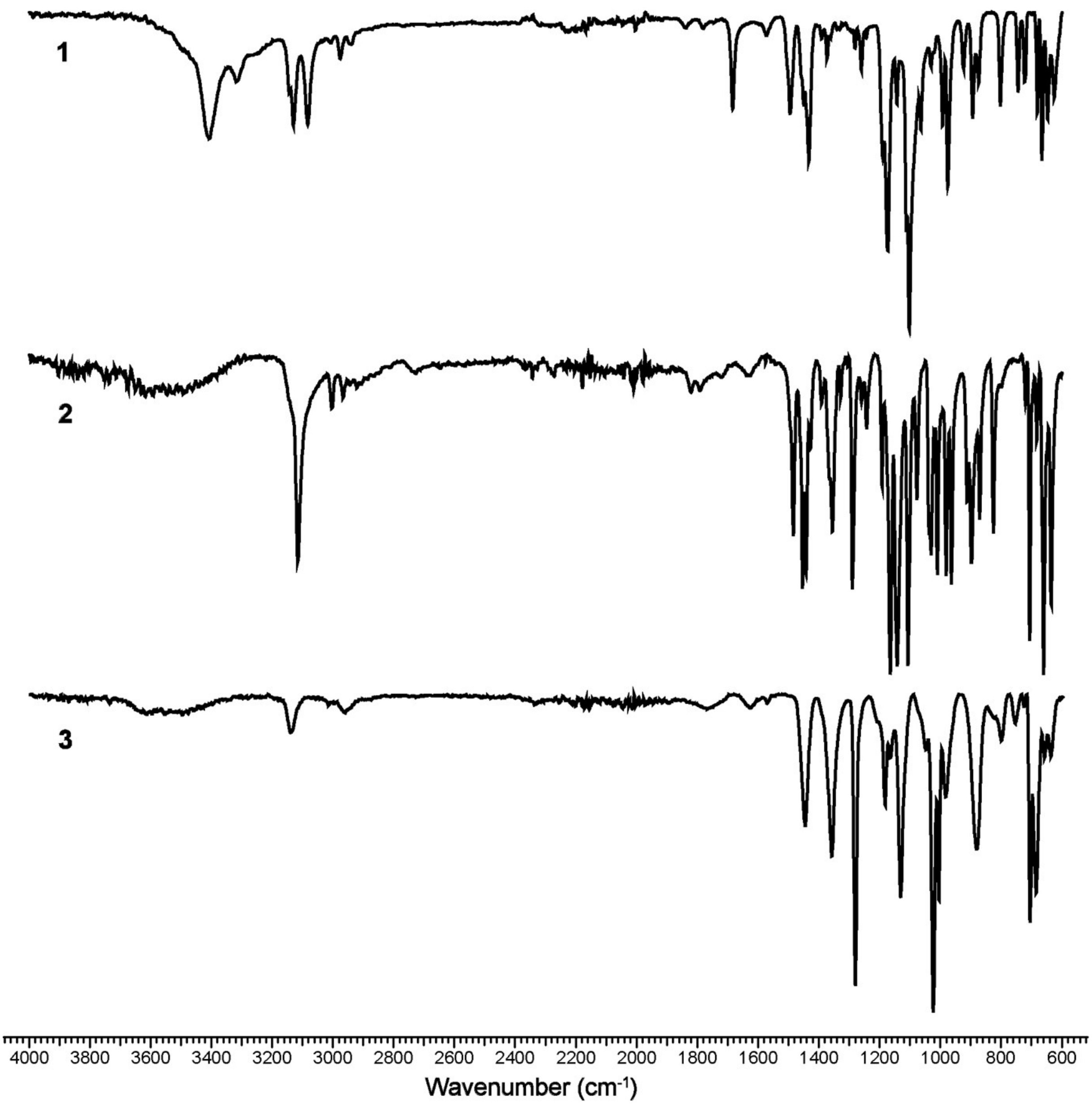


Figure S1 Infrared spectra of **1**–**3**.

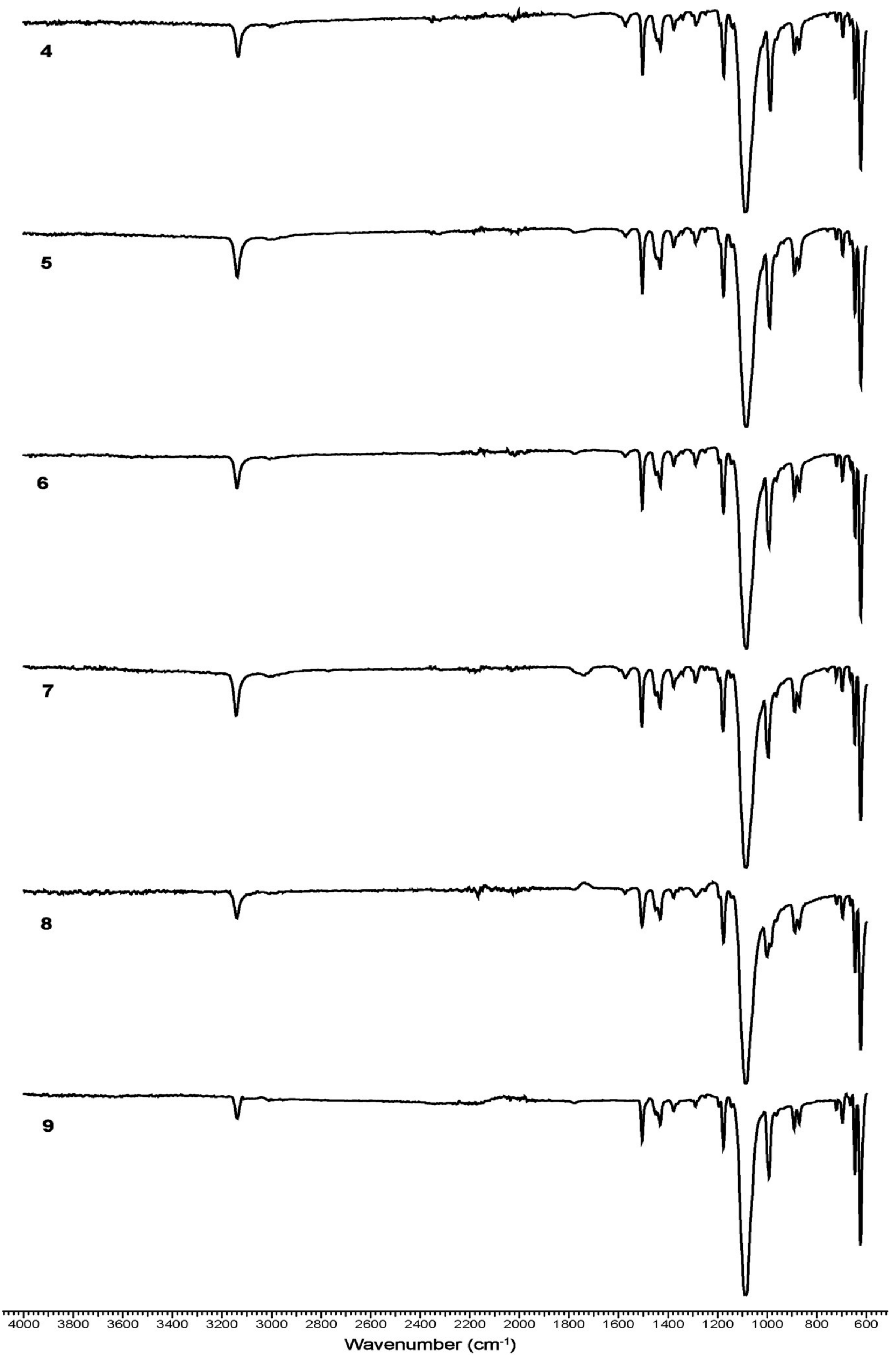


Figure S2 Infrared spectra of **4**–**9**.

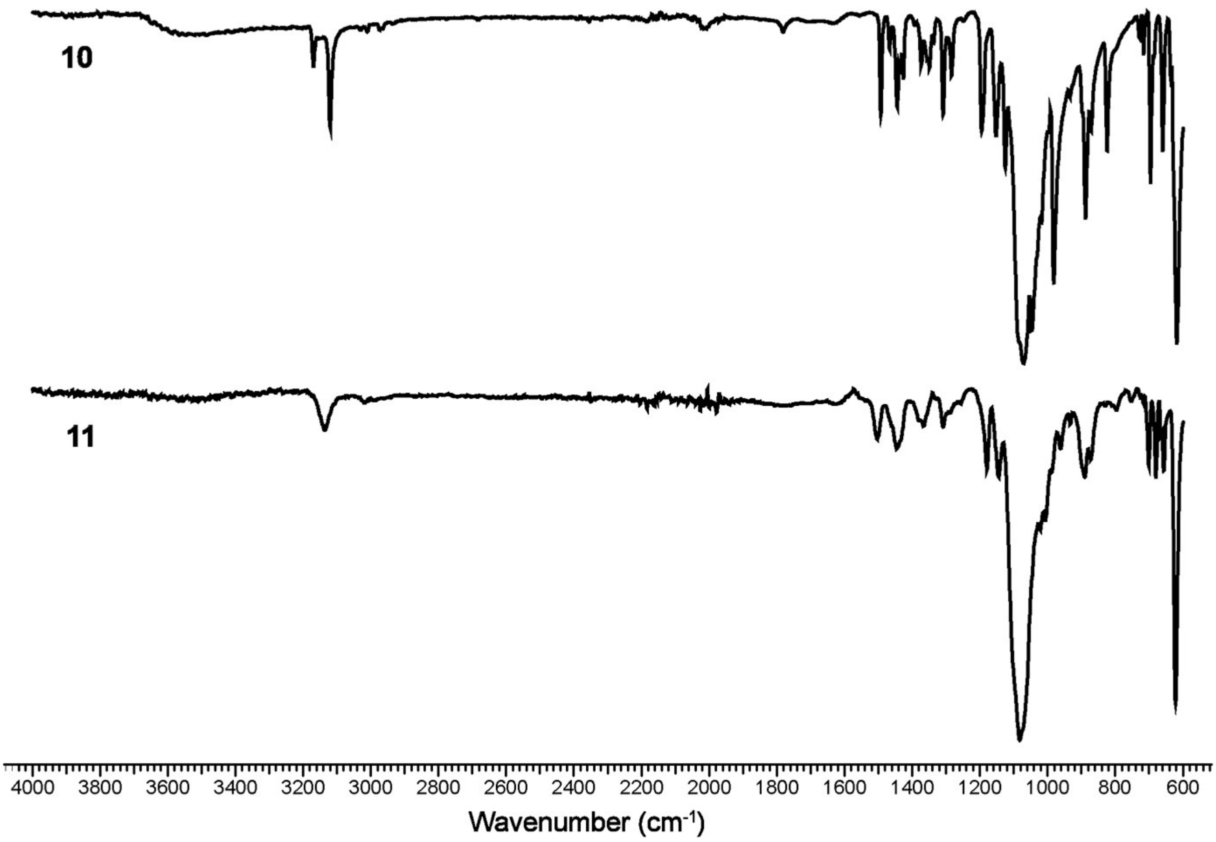


Figure S3 Infrared spectra of **10** and **11**.

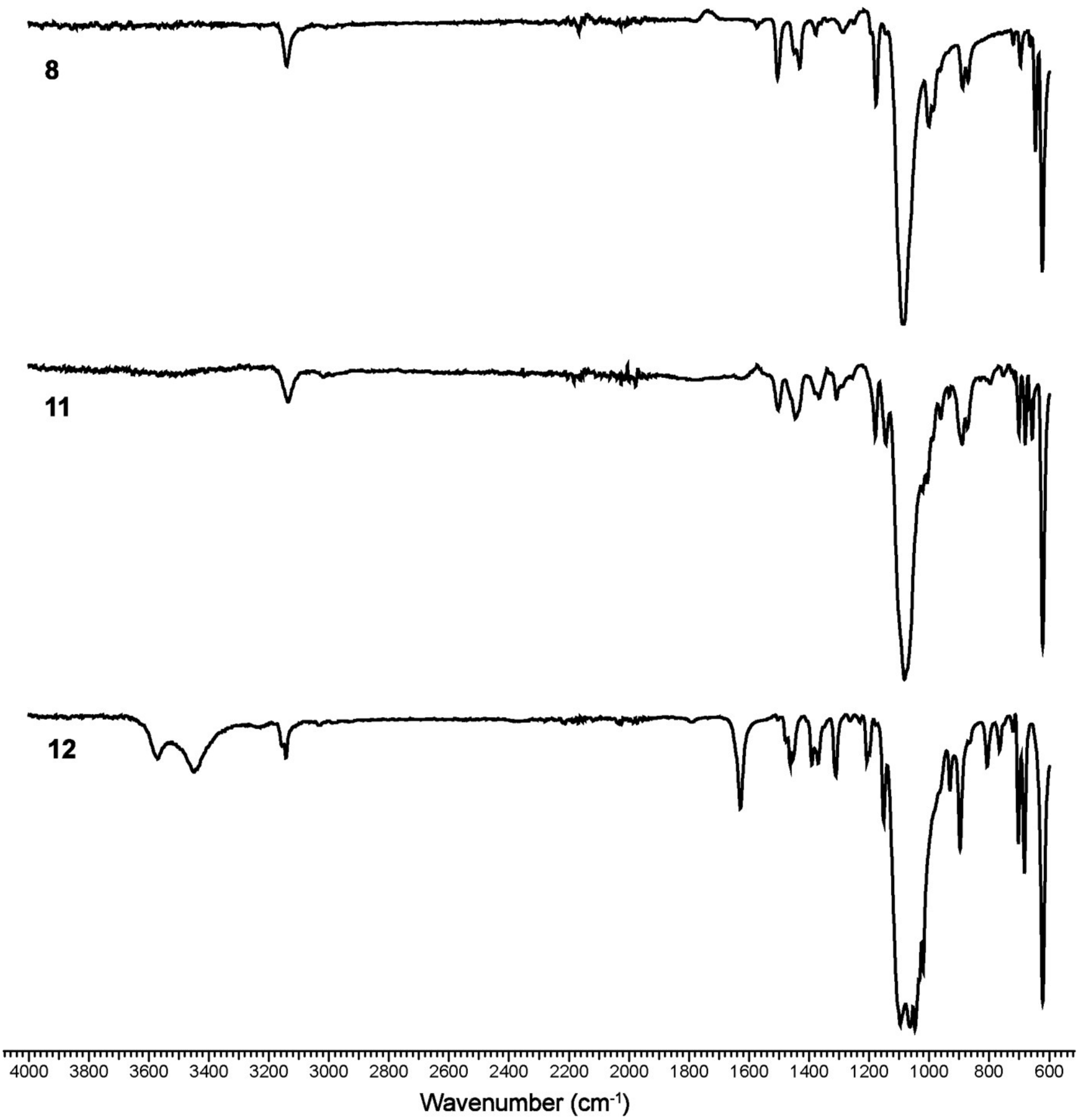


Figure S4 Infrared spectra of **8** and **11**/**12**.

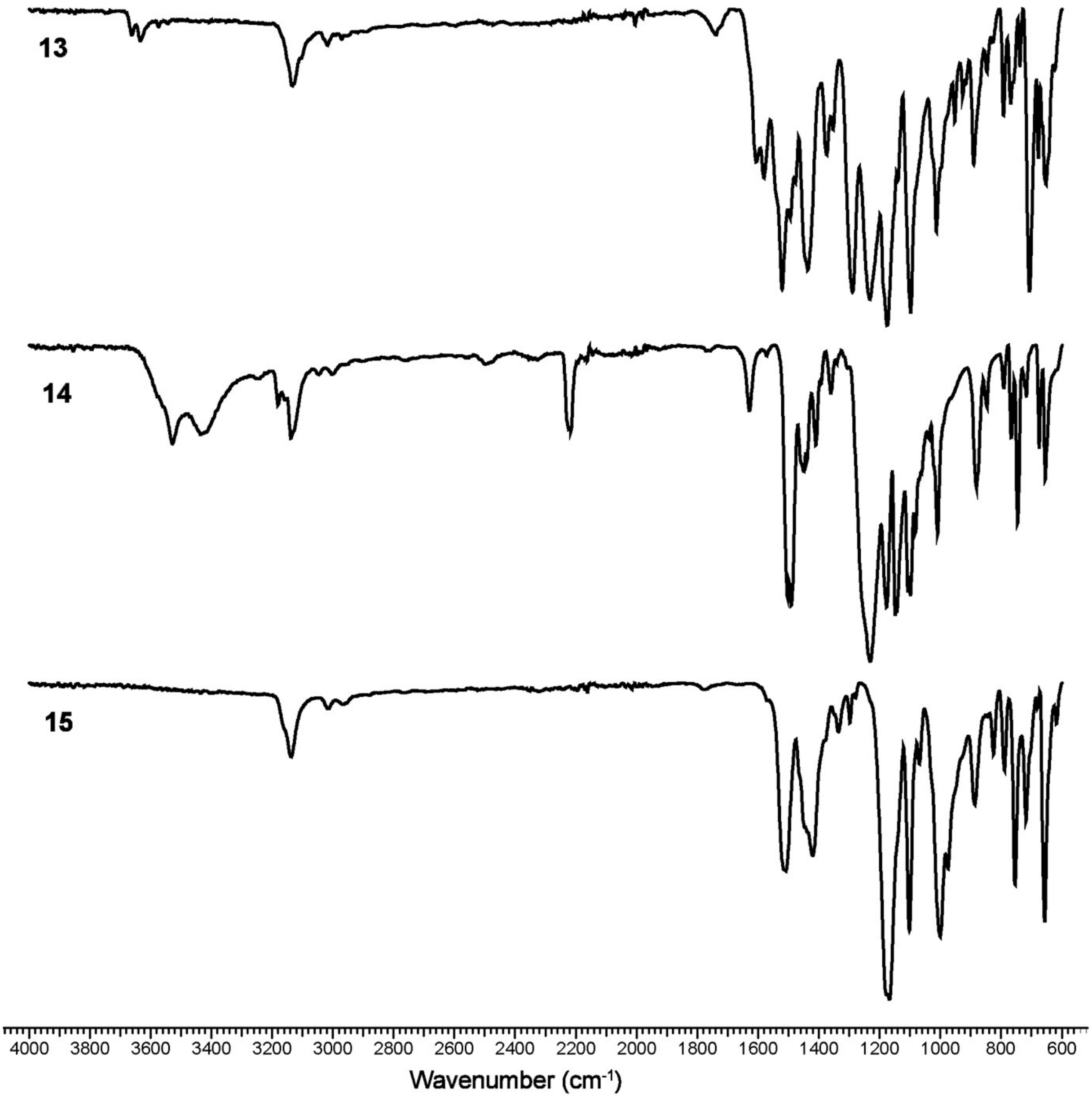


Figure S5 Infrared spectra **13**–**15**.

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 (λ = 0.7107 Å). On the Oxford device, data collection and reduction were carried out using the CRYSALISPRO 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] or SHELXS-97[S4]) and refined by full-matrix least-squares on *F*2 (SHELXL[S4]) and finally checked using the PLATON software[S5] integrated in the WinGX[S6] 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[S7,8]. All DIAMOND2 plots are shown with thermal ellipsoids at the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius.

Table S1. Crystallographic data of **1**–**5**.

	1	**2**	**3**	**4**	**5**
Formula	$C_5H_{10}N_8O$	$C_5H_8N_8$	$C_5H_8N_8$	$C_{15}H_{24}Cl_2MnN_{24}O_8$	$C_{15}H_{24}Cl_2FeN_{24}O_8$
FW [g mol^{-1}]	198.19	180.18	180.18	794.36	795.26
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Trigonal	Trigonal
Space Group	$Pbca$	$P2_1/n$	$P2_1/c$	$P{-}3c1$	$P{-}3c1$
Color / Habit	Colorless block	Colorless block	Colorless block	Colorless block	Yellow block
Size [mm]	0.38 x 0.54 x 0.59	0.31 x 0.41 x 0.42	0.11 x 0.33 x 0.47	0.23 x 0.37 x 0.66	0.11 x 0.14 x 0.21
a [Å]	10.2283(10)	10.6063(6)	11.6710(6)	11.1661(2)	10.9450(4)
b [Å]	10.9670(12)	6.5631(4)	4.7586(2)	11.1661(2)	10.9450(4)
c [Å]	16.3177(15)	11.7632(7)	15.1639(7)	14.7523(4)	14.5170(5)
α [°]	90	90	90	90	90
β [°]	90	90.685(5)	105.362(5)	90	90
γ [°]	90	90	90	120	120
V [Å^3]	1830.4(3)	818.78(8)	812.08(7)	1592.92(8)	1506.05(14)
Z	8	4	4	2	2
$\rho_{calc.}$ [g cm^{-3}]	1.439	1.462	1.474	1.656	1.754
μ [mm^{-1}]	0.111	0.107	0.108	0.665	0.765
F(000)	832	376	376	810	812
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71069
T [K]	173	173	143	173	123
θ Min–Max [°]	4.4, 26.0	4.7, 26.0	4.5, 26.0	4.2, 26.0	4.3, 26.3
Dataset	−10: 12; −13: 13; −20: 19	−13: 12; −7: 8; −14: 14	−13: 14; −5: 5; −17: 18	−13: 13; −13: 13; −18: 18	−13: 13; −13: 13; −18: 17
Reflections collected	13404	6419	5707	11705	11272
Independent refl.	1792	1598	1588	1036	1032
R_{int}	0.034	0.020	0.022	0.022	0.039
Observed reflections	1485	1387	1370	925	873
Parameters	167	150	118	98	101
R_1 (obs)[a]	0.0301	0.0310	0.0319	0.0292	0.0304
wR_2 (all data)[b]	0.0772	0.083	0.0805	0.0825	0.080
GooF[c]	1.04	1.05	1.04	1.08	1.07
Resd. Dens. [e Å^{-3}]	−0.19, 0.19	−0.28, 0.17	−0.22, 0.15	−0.34, 0.40	−0.39, 0.56
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
CCDC	1816637	1816632	1816632	1816628	1816635

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).

Table S2. Crystallographic data of **6** and **8–11**.

	6	**8**	**9**	**10**	**11**
Formula	$C_{12}H_{28}CoN_{26}O_8$	$C_{15}H_{24}Cl_2CuN_{24}O_8$	$C_{15}H_{24}Cl_2N_{24}O_8Zn$	$C_5H_8AgClN_8O_4$	$C_{15}H_{24}Cl_2CuN_{24}O_8$
FW [g mol^{-1}]	798.41	802.96	804.80	387.49	802.96
Crystal system	Triclinic	Trigonal	Trigonal	Monoclinic	Triclinic
Space Group	$P-3c1$	$P-3c1$	$P-3c1$	$P2_1/c$	$P-1$
Color / Habit	Orange block	Blue block	Colorless block	Colorless block	Blue rod
Size [mm]	0.06 x 0.07 x 0.10	0.18 x 0.27 x 0.28	0.23 x 0.37 x 0.50	0.10 x 0.20 x 0.46	0.16 x 0.19 x 0.24
a [Å]	11.085(5)	11.061(5)	11.0824(3)	9.8070(2)	13.2260(6)
b [Å]	11.085 (5)	11.061(5)	11.0824(3)	10.7250(2)	13.7860(8)
c [Å]	14.554(5)	14.622(5)	14.7279(8)	11.1830(3)	20.2220(8)
α [°]	90	90	90	90	99.253(4)
β [°]	90	90	90	105.128(2)	102.001(4)
γ [°]	120	120	120	90	114.596(5)
V [Å^3]	1548.8(17)	1549.3(17)	1566.53(14)	1135.47(5)	3150.0(3)
Z	2	2	2	4	2
$\rho_{calc.}$ [g cm^{-3}]	1.712	1.721	1.706	2.267	1.693
μ [mm^{-1}]	0.811	0.962	1.038	2.039	0.947
F(000)	814	818	820	760	1636
$\lambda_{MoK\alpha}$ [Å]	0.71069	0.71069	0.71073	0.71069	0.71069
T [K]	173	123	173	123	123
θ Min–Max [°]	3.5, 26.0	4.6, 26.2	4.2, 32.4	4.2, 26.0	4.2, 26.0
Dataset	−13: 13; −13:13; −17: 16	−11: 13; −13: 13; −18: 15	−16: 15; −15: 16; −21: 21	−12: 12; −12: 13; −13: 13	−16: 16; −11:17; −24: 24
Reflections collected	13757	11267	15991	8392	22717
Independent refl.	1023	1037	1815	2218	12300
R_{int}	0.045	0.041	0.057	0.020	0.041
Observed reflections	918	828	1210	2071	9173
Parameters	99	103	97	204	925
R_1 (obs)[a]	0.0309	0.0329	0.0397	0.0170	0.0651
wR_2 (all data)[b]	0.0823	0.0927	0.1050	0.0413	0.1860
GooF[c]	1.09	1.10	1.02	1.04	1.03
Resd. Dens. [e Å^{-3}]	−0.38, 0.54	−0.24, 0.51	−0.37, 0.54	−0.39, 0.45	−0.94 / 2.98
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
CCDC	1816627	1816626	1816629	1816630	1816636

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).

Table S3. Crystallographic data of **12**, **14** and **15**.

	12	**14**	**15**
Formula	$C_{10}H_{20}Cl_2CuN_{16}O_{10}$	$C_{14}H_{20}CuN_{22}O_{10}$	$C_{15}H_{24}CuN_{30}O_8$
FW [g mol^{-1}]	658.86	720.06	816.11
Crystal system	Monoclinic	Triclinic	Monoclinic
Space Group	$P2_1/c$	$P{-}1$	$C2/c$
Color / Habit	Blue block	Blue block	Blue platelet
Size [mm]	0.10 x 0.25 x 0.30	0.28 x 0.40 x 0.60	0.02 x 0.04 x 0.10
a [Å]	8.4824(4)	9.4670(5)	27.0187(10)
b [Å]	14.4398(5)	10.3140(5)	18.5080(6)
c [Å]	10.7195(5)	14.0761(7)	15.4569(5)
α [°]	90	90.390(4)	90
β [°]	109.217	92.808(4)	124.910(1)
γ [°]	90	98.412(4)	90
V [Å^3]	1239.81(10)	1357.87(12)	6338.5(4)
Z	2	2	8
$\rho_{calc.}$ [g cm^{-3}]	1.765	1.761	1.711
μ [mm^{-1}]	1.178	0.900	0.784
F(000)	670	734	3336
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	233	123	103
θ Min–Max [°]	4.2, 26.2	4.6, 26.0	2.5, 26.0
Dataset	−10: 10; −17: 17; −13: 13	−11: 11; −12: 12; −17: 17	−33: 33; −22: 22; −19: 17
Reflections collected	18445	11012	46253
Independent refl.	2490	5316	6221
R_{int}	0.033	0.023	0.043
Observed reflections	2224	4356	5166
Parameters	246	449	562
R_1 (obs)[a]	0.0395	0.0293	0.0283
wR_2 (all data)[b]	0.1110	0.0735	0.0774
GooF[c]	1.06	1.03	1.05
Resd. Dens. [e Å^{-3}]	−0.67, 0.83	−0.38, 0.45	−0.55, 0.35
Absorption correction	multi-scan	multi-scan	multi-scan
CCDC	1816633	1816631	1816634

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).

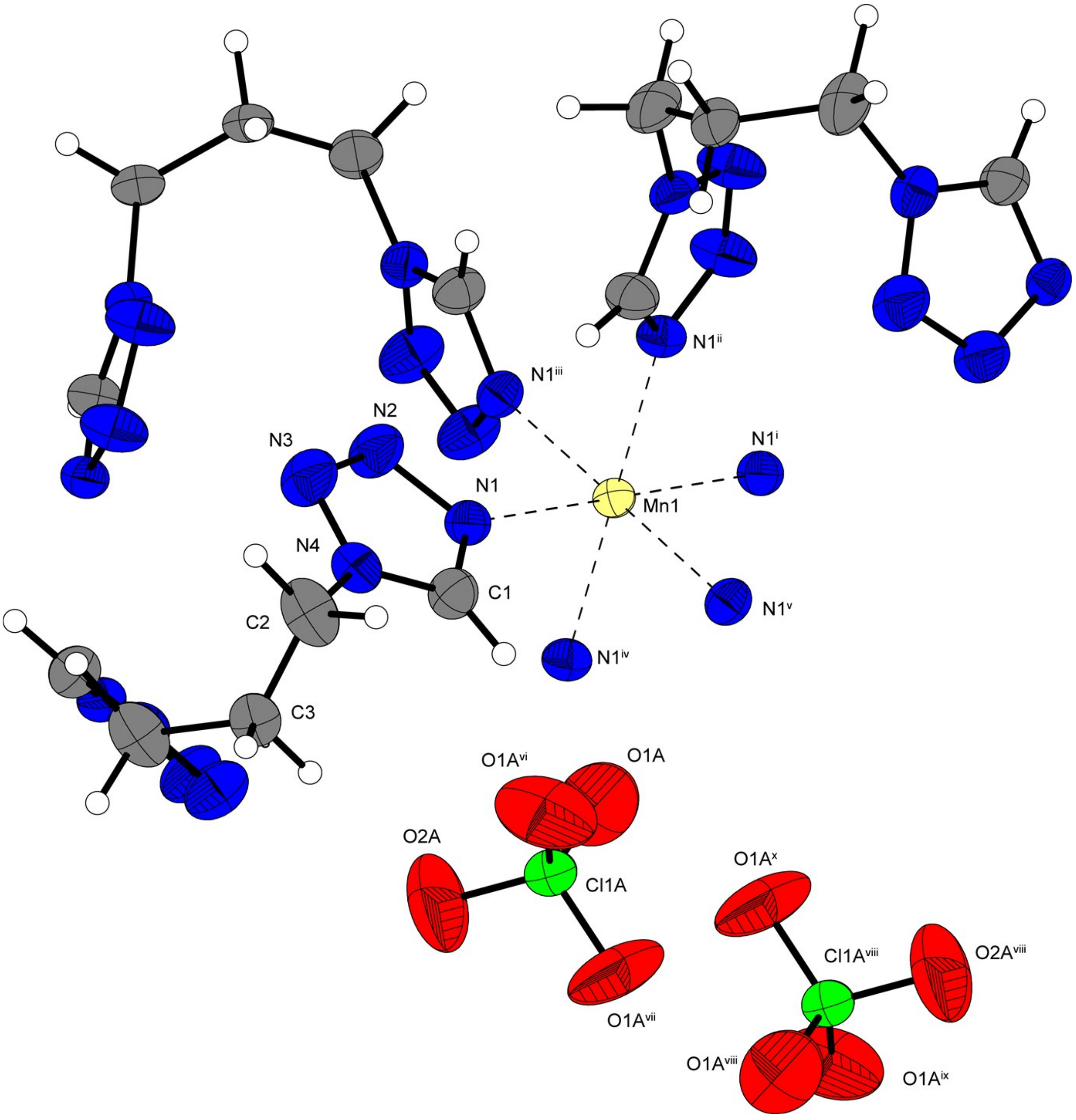


Figure S6 Manganese(II) coordination environment of [Mn(1,1-dtp)$_3$](ClO$_4$)$_2$ (**4**). Selected bond length (Å): Mn1–N1 2.2533(13); selected bond angles (°): N1–Mn1–N1^{i} 180.00, N1–Mn1–N1^{iii} 91.25(5), and N1–Mn1–N1^{v} 88.76(5). Symmetry codes: (i) –x, −y, −z; (ii) x−y, x, −z; (iii) –y, x−y, z; (iv) –x+y, −x, z; (v) y, −x+y, −z; (vi) 1−x+y, 1−x, z; (vii) 1−y, x−y, z; (viii) 1−x, −y, −z; (ix) x−y, −1+x, −z; (x) y, −x+y, −z.

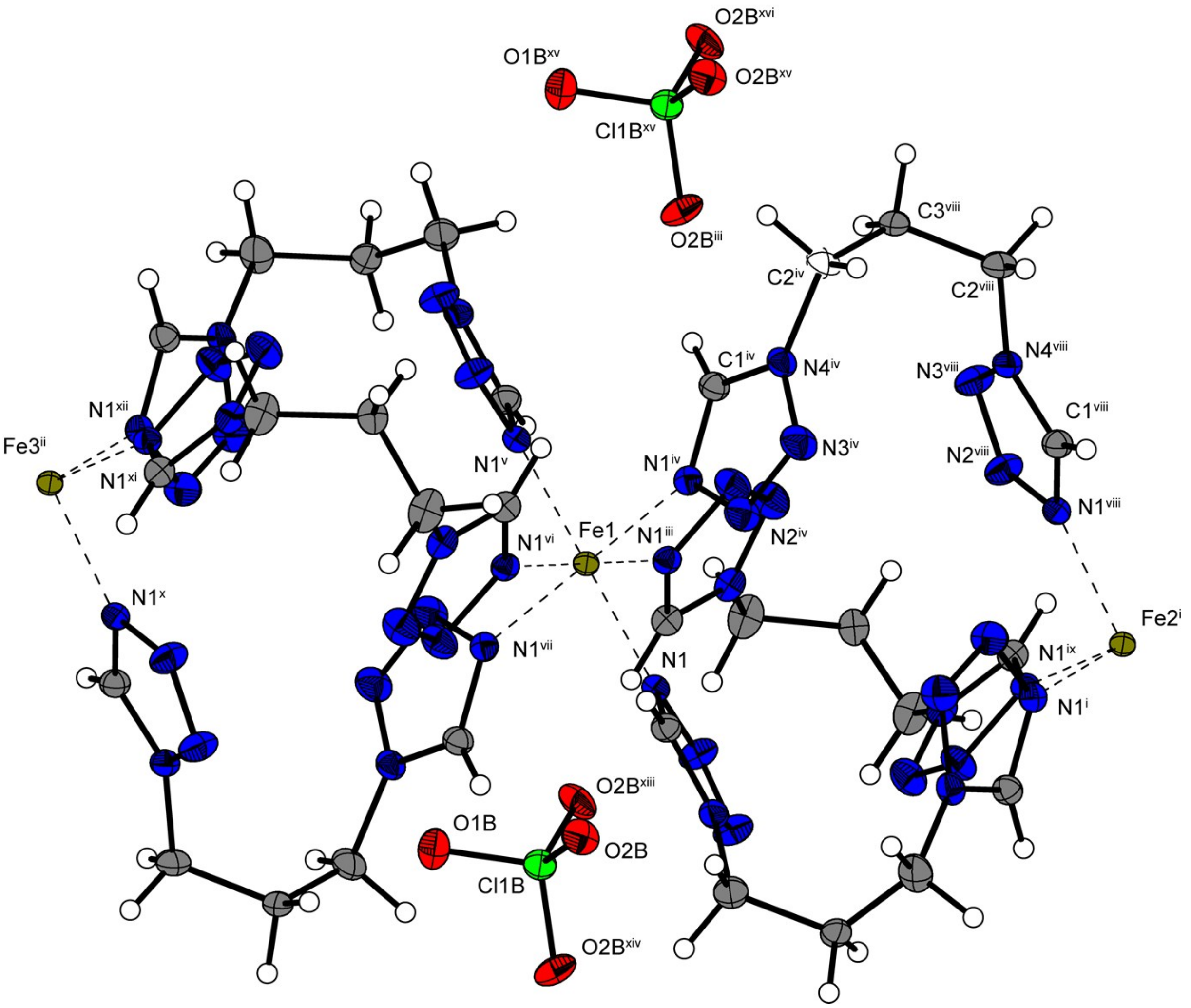


Figure S7 Complex unit of [Fe(1,1-dtp)$_3$](ClO$_4$)$_2$ (**5**). Selected bond length (Å): Fe1–N1 1.9950(17); selected bond angles (°): N1–Fe1–N1^{iii} 90.55(7), N1–Fe1–N1^{v} 180.00, and N1–Fe1–N1^{iv} 89.45(7). Symmetry codes: (i) x−y, −y, 0.5−z; (ii) x−y, −y, 0.5−z; (iii) –y, x−y, z; (iv) –x+y, −x, z; (v) –x, −y, −z; (vi) y, −x+y, −z; (vii) x−y, x, −z; (viii) –x, −x+y, 0.5−z; (ix) y, x, 0.5−z; (x) x, x−y, −0.5+z; (xi) –y, −x, −0.5+z; (xii) –x+y, y, −0.5+z; (xiii) –x+y, 1−x, z; (xiv) 1−y, 1+x−y, z; (xv) −1+x, −1+y, z; (xvi) −1−x+y, −x, z.

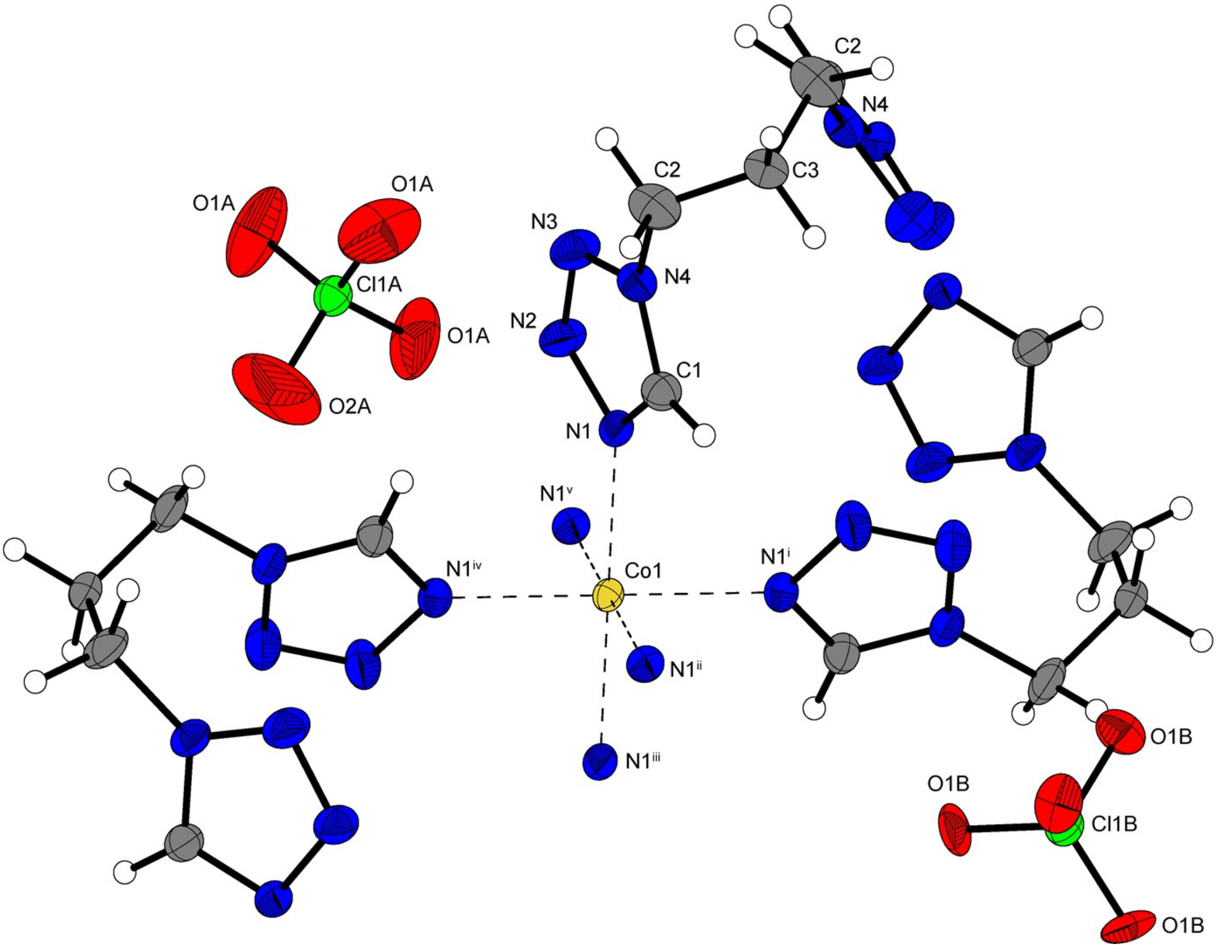


Figure S8 Cobalt(II) coordination environment of $[Co(1,1\text{-dtp})_3](ClO_4)_2$ (**6**). Selected bond length (Å): Co1–N1 2.1399(17). selected bond angles (°): N1–Co1–N1^{i} 91.19(6), N1–Co1–N1^{iii} 180.00, and N1–Zn1–N1^{ii} 88.81(7). Symmetry codes: (i) −y, x−y, z; (ii) x−y, x, 1−z; (iii) –x, −y, 1−z; (iv) y, −x+y, 1−z; (v) –x+y, −x, z.

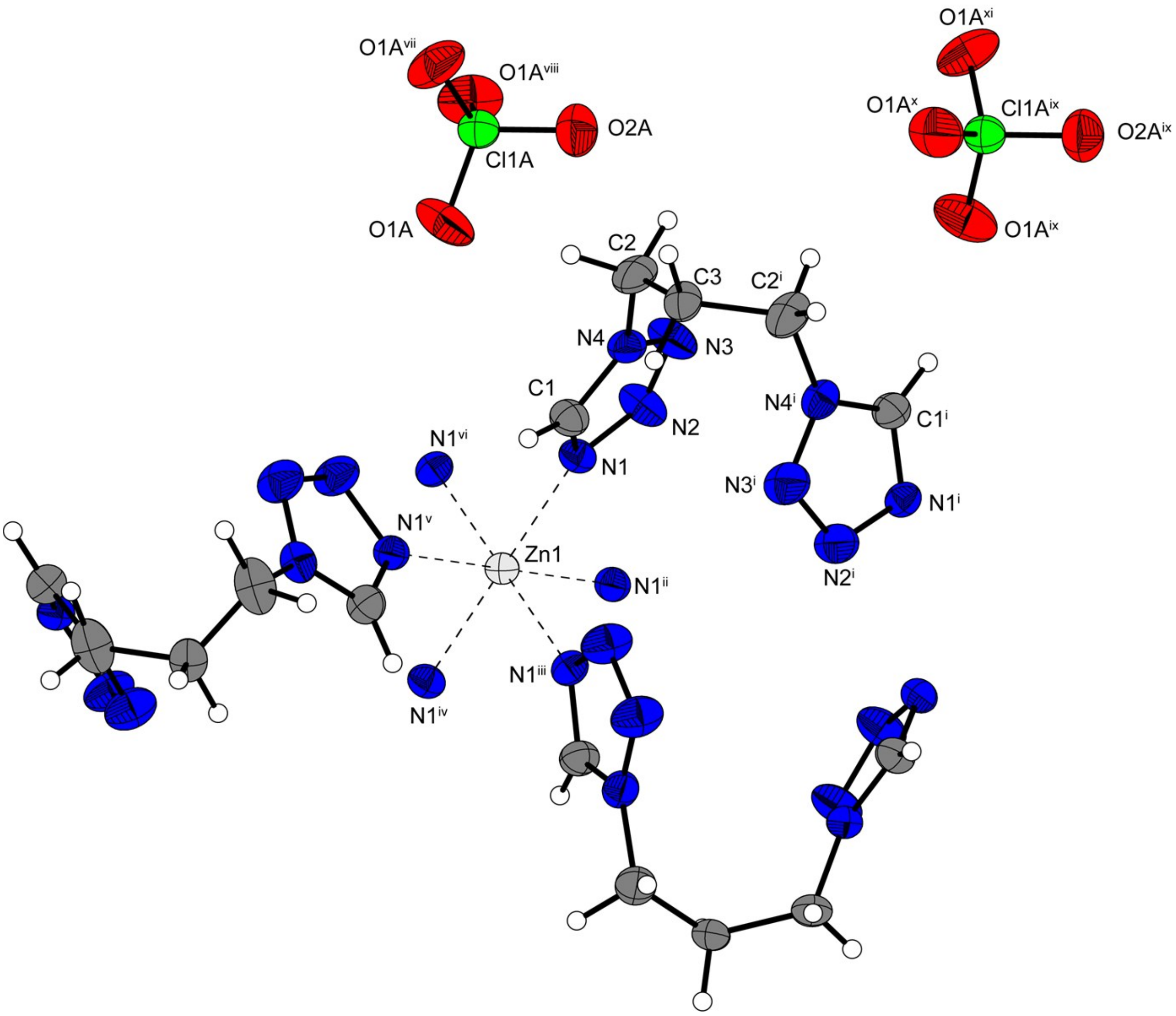


Figure S9 Zinc(II) coordination environment of $[Zn(1,1\text{-dtp})_3](ClO_4)_2$ (**9**). Selected bond length (Å): Zn1–N1 2.1647(15). selected bond angles (°): N1–Zn1–N1^{ii} 90.80(7), N1–Zn1–N1^{iv} 180.00, and N1–Zn1–N1^{vi} 89.20(7). Symmetry codes: (i) −x, −x+y, 0.5−z; (ii) –x+y, −x, z; (iii) –y, x−y, z; (iv) –x, −y, −z; (v) x−y, x, −z; (vi) y, −x+y, −z; (vii) –x+y, 1−x, z; (viii) 1−y, 1+x−y, z; (ix) –x+y, y, 0.5+z; (x) x, 1+x−y, 0.5+z; (xi) 1−y, 1−x, 0.5+z.

Complex **13** (Figure S10) shows an octahedral coordination sphere with a molecular unit containing one bidentate ditetrazole ligand and a tetradentate styphnate dianion (via the nitro- and deprotonated hydroxy groups). Bridging between the copper(II) metal centers through all ligands leads to the formation of polymeric chains.

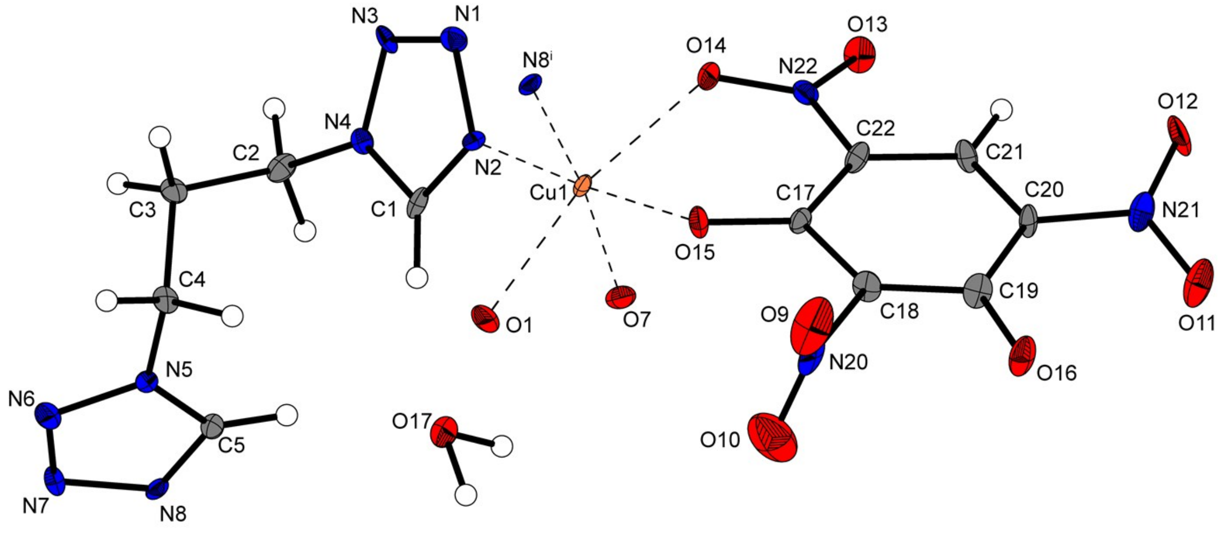


Figure S10 Copper(II) coordination environment of [Cu(TNR)(1,1-dtp)] · H_2O (**13**).

4. DTA plots of 1–3, 8 and 10–15

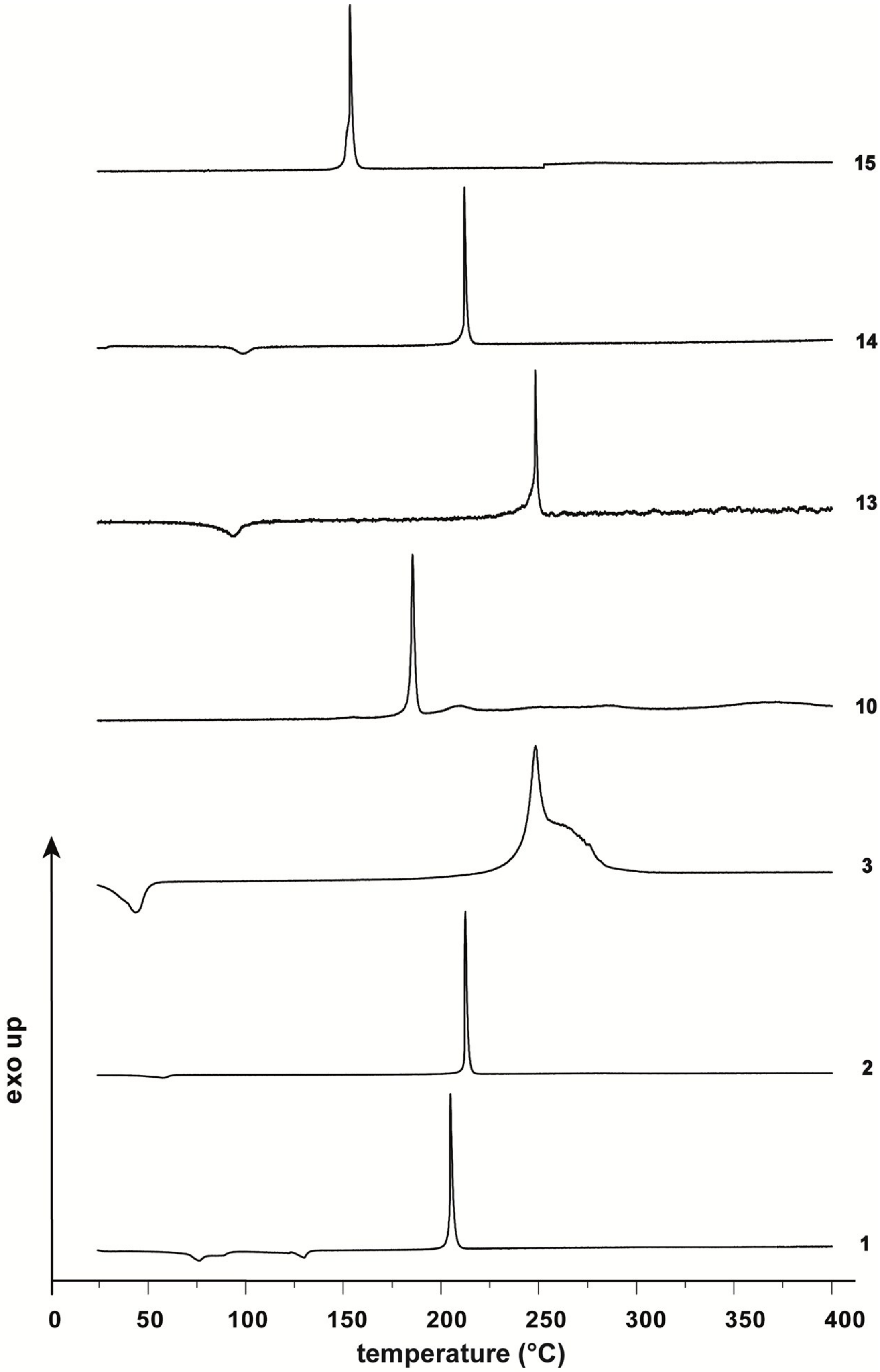


Figure S11 DTA plots of **1–3**, **10** and **13–15**.

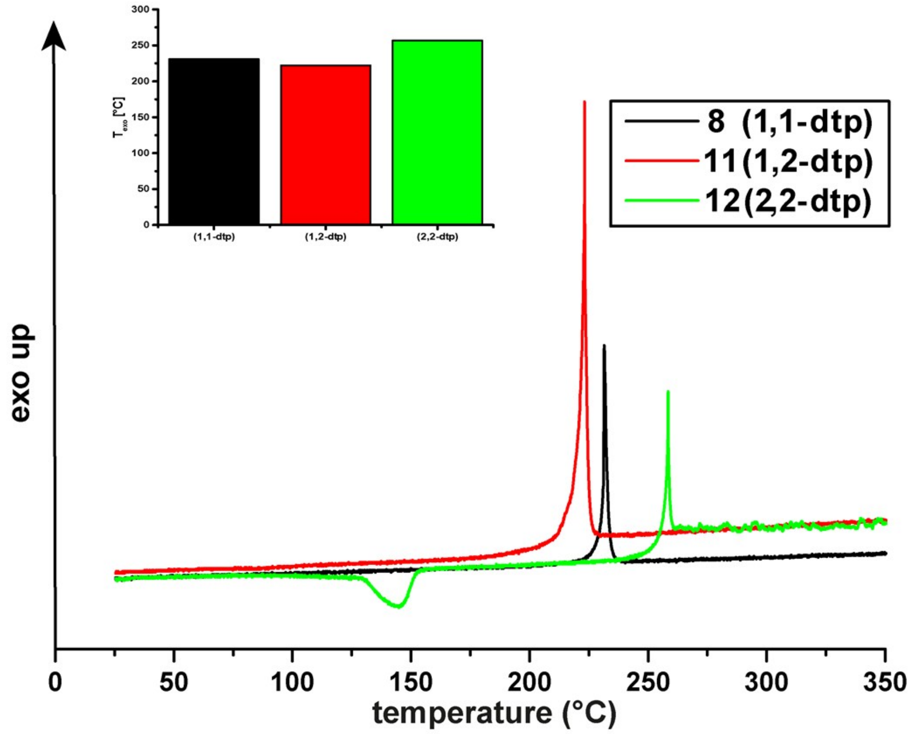


Figure S12 DTA plot (5 °C min^{-1}) comparison of the different dtp isomer containing copper(II) perchlorate complexes **8**, **11** and **12**.

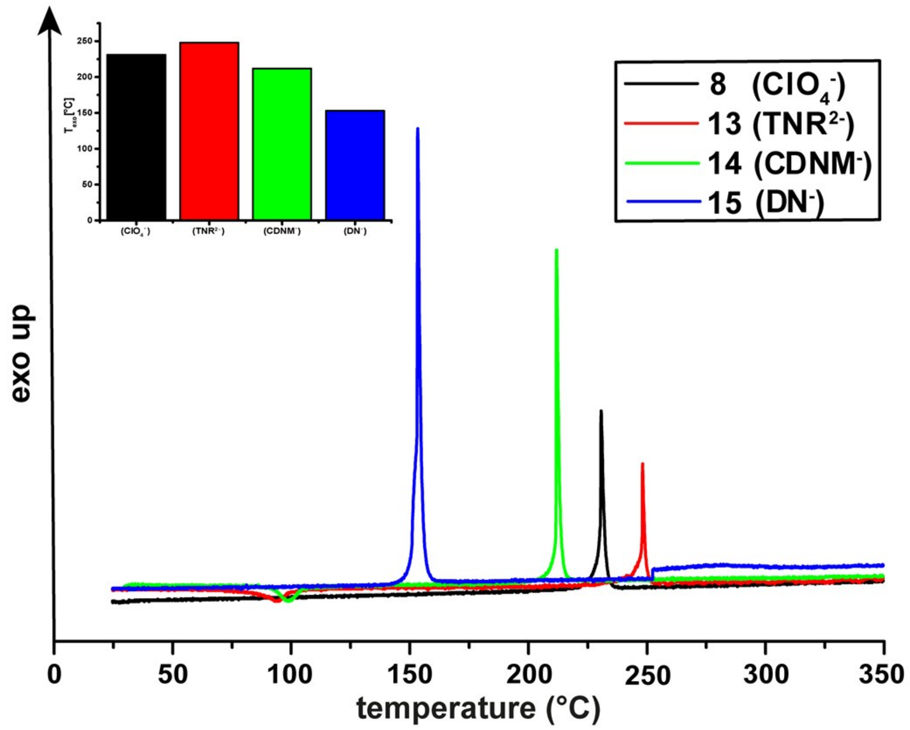


Figure S13 DTA plot (5 °C min^{-1}) comparison of the different 1,1-dtp based copper(II) complexes **8** and **13**–**15** with varying anions.

5. Column diagrams of the complexes of **8** and **11–15**

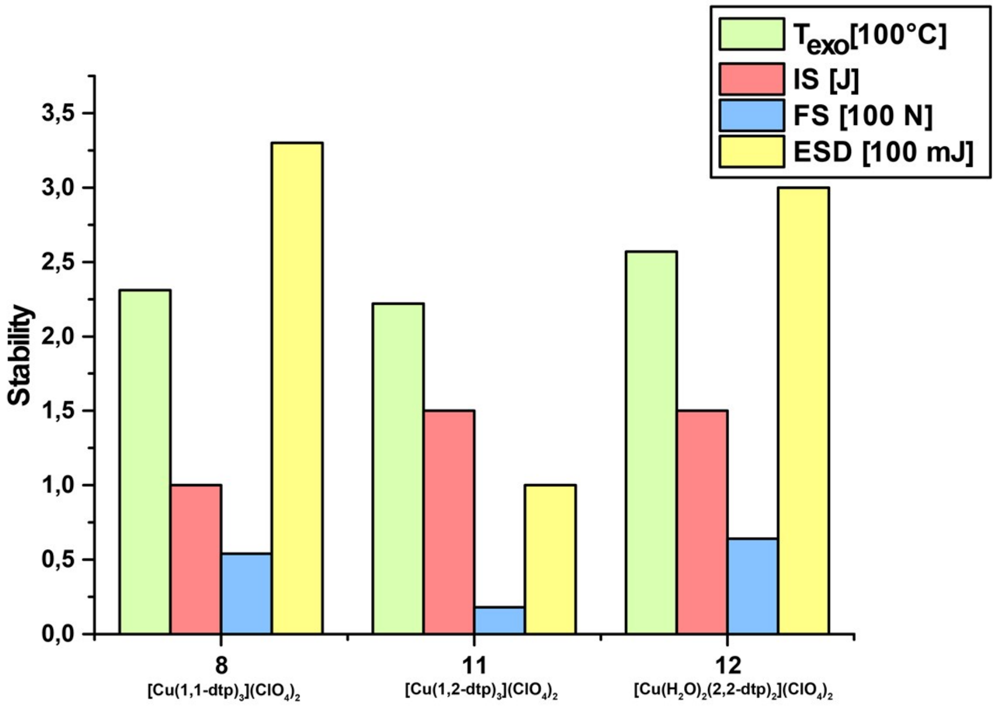


Figure S14 Stabilities of the copper(II) perchlorate complexes **8**, **11** and **12**.

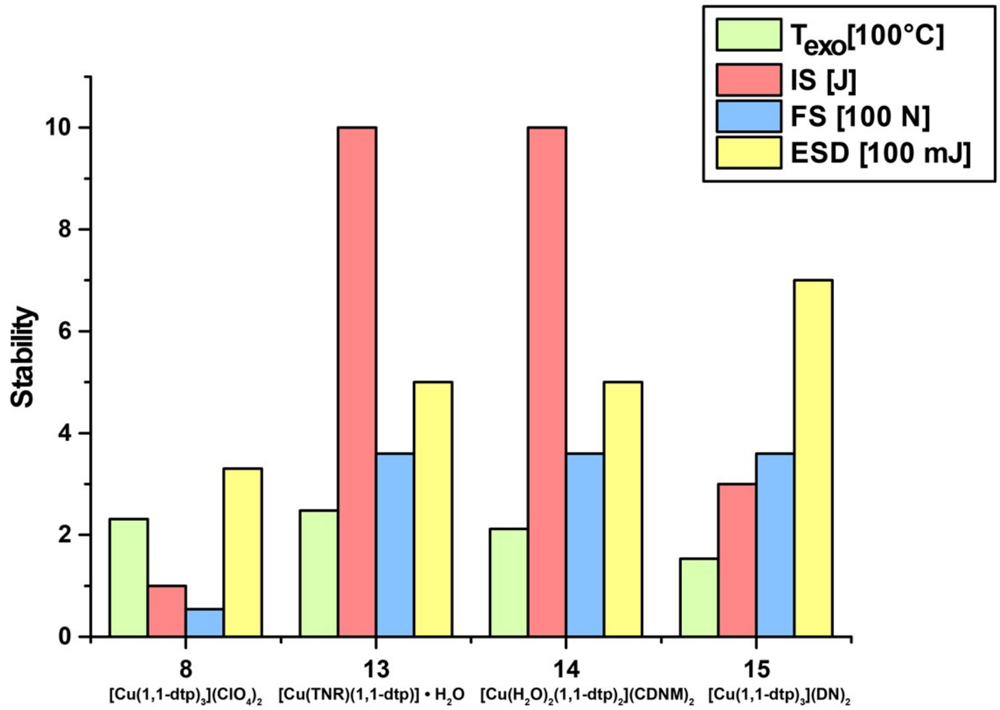


Figure S15 Stabilities of the copper(II) 1,1-dtp containing complexes **8** and **13–15**.

6. Hot plate and hot needle tests

Figure S16 Moment of deflagration of complex **11** during the hot plate test.

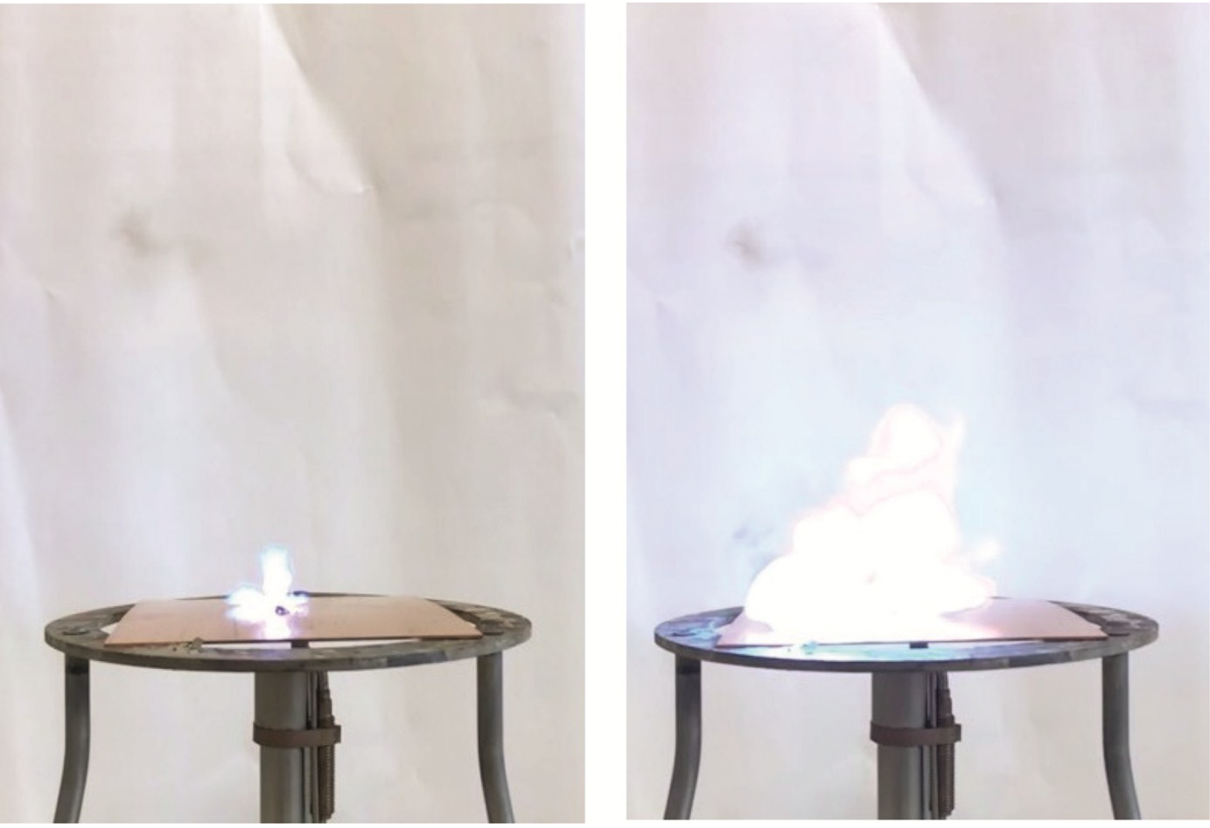


Figure S17 Moment of deflagration during the hot plate test for compound **12** shown as sequence.

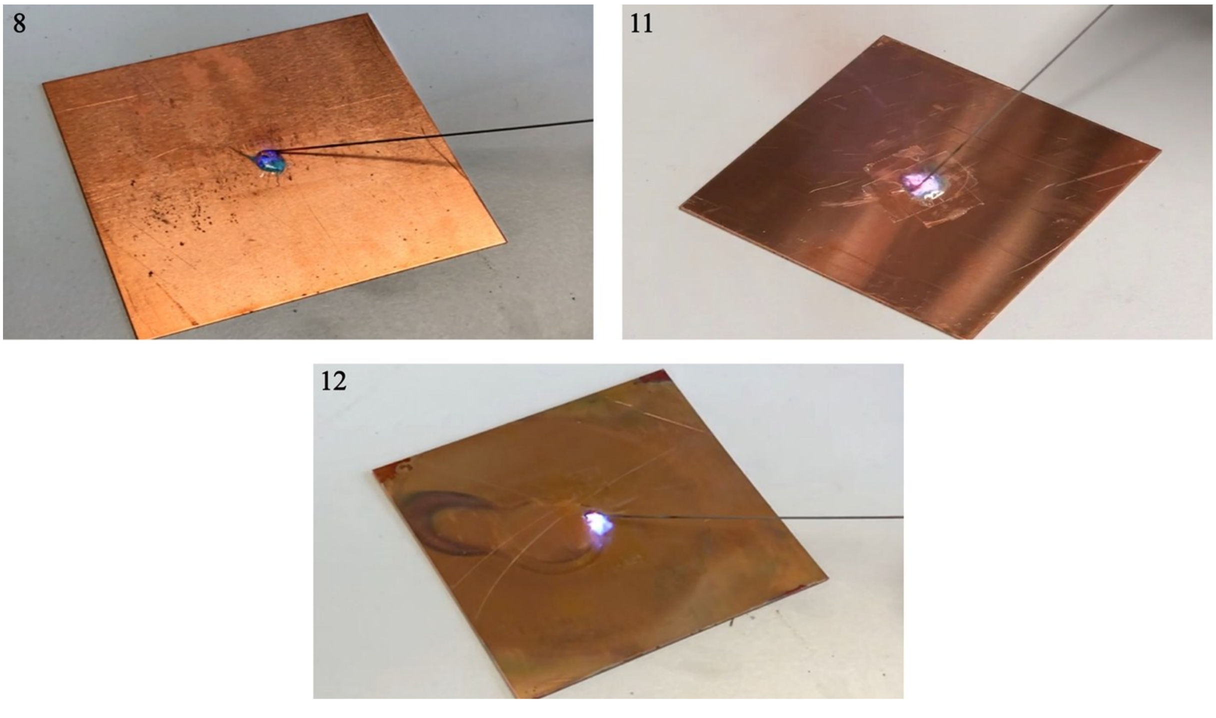


Figure S18 Deflagrations of **8, 11** and **12** during the hot plate ignition tests.

7. Laser ignition tests

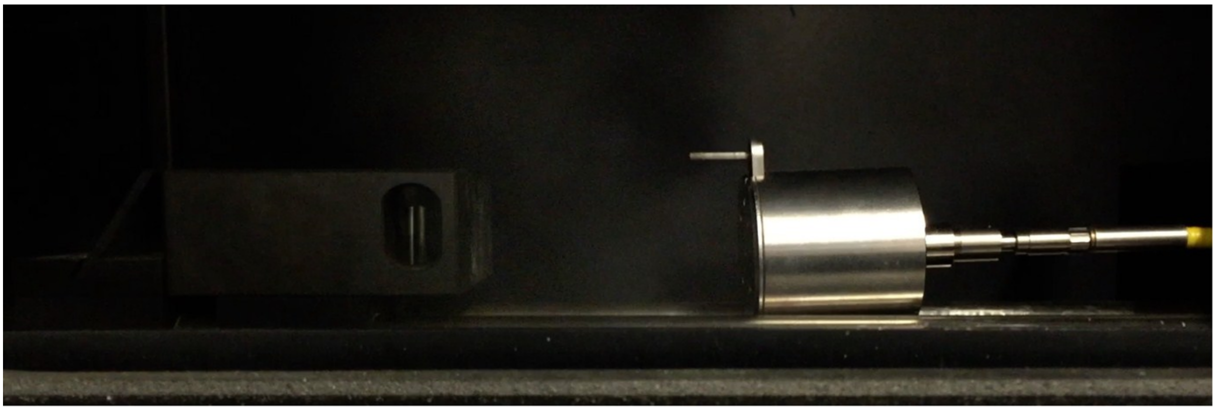


Figure S19 Detonation of **11** during the laser initiation test.

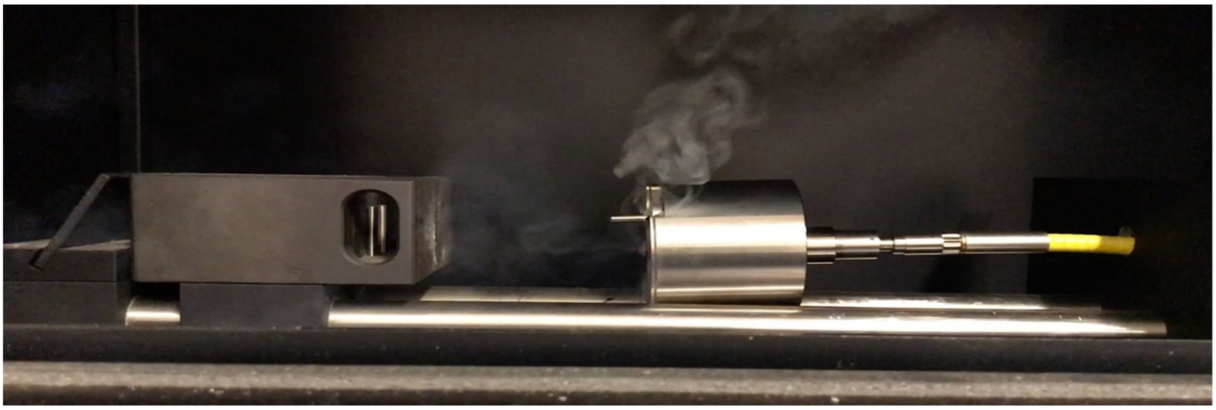


Figure S20 Decomposition of **13** as reaction to laser irradiation.

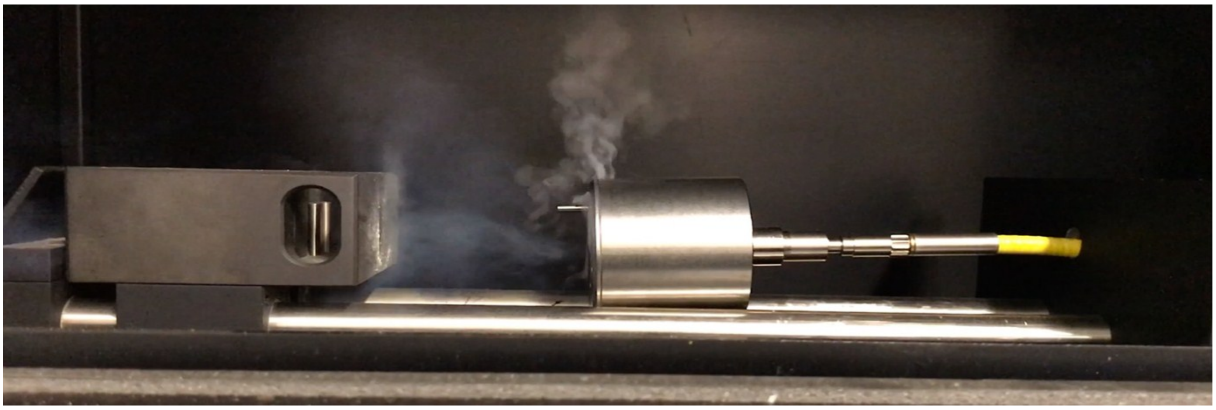


Figure S21 Moment of deflagration of complex **14**.

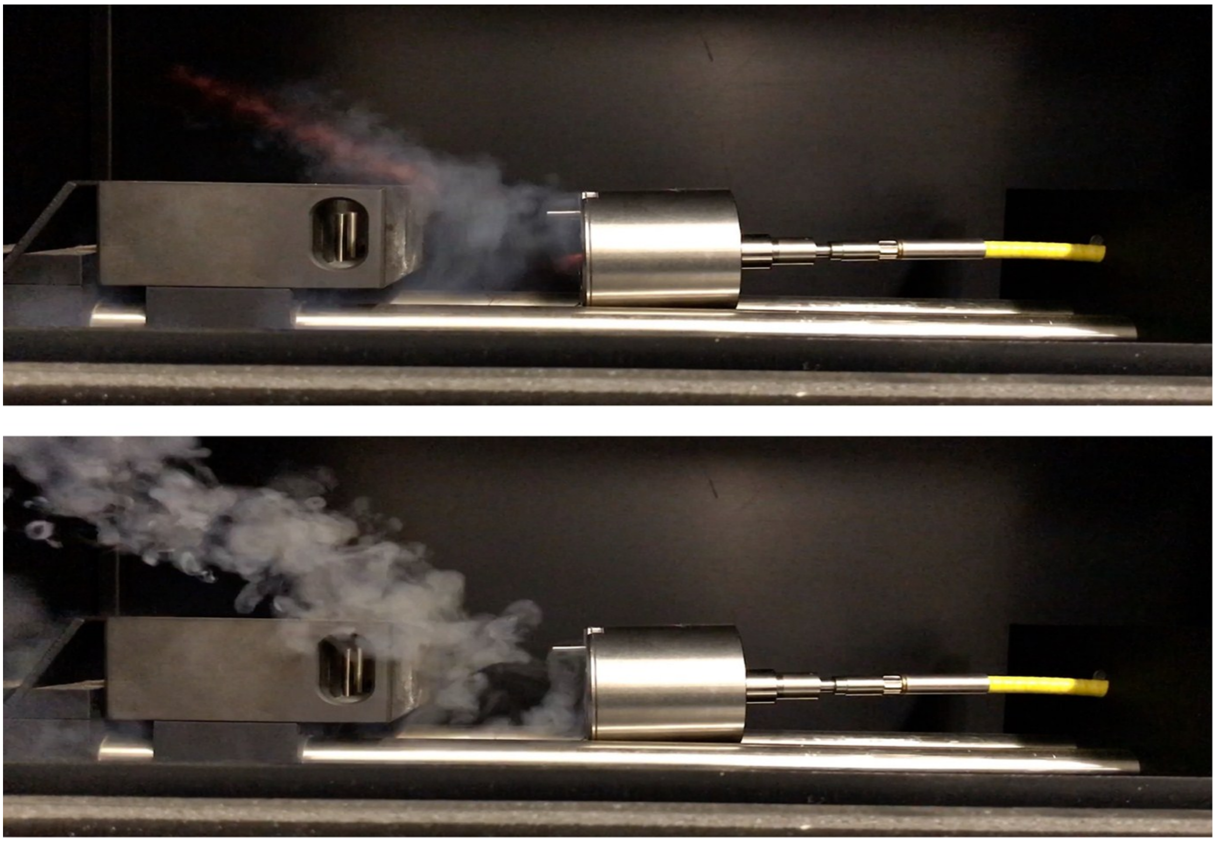


Figure S22 Deflagration reaction of complex **15** shown as sequence during laser initiation experiments.

8. UV-Vis spectra of 4, 9, 10 and 13–15

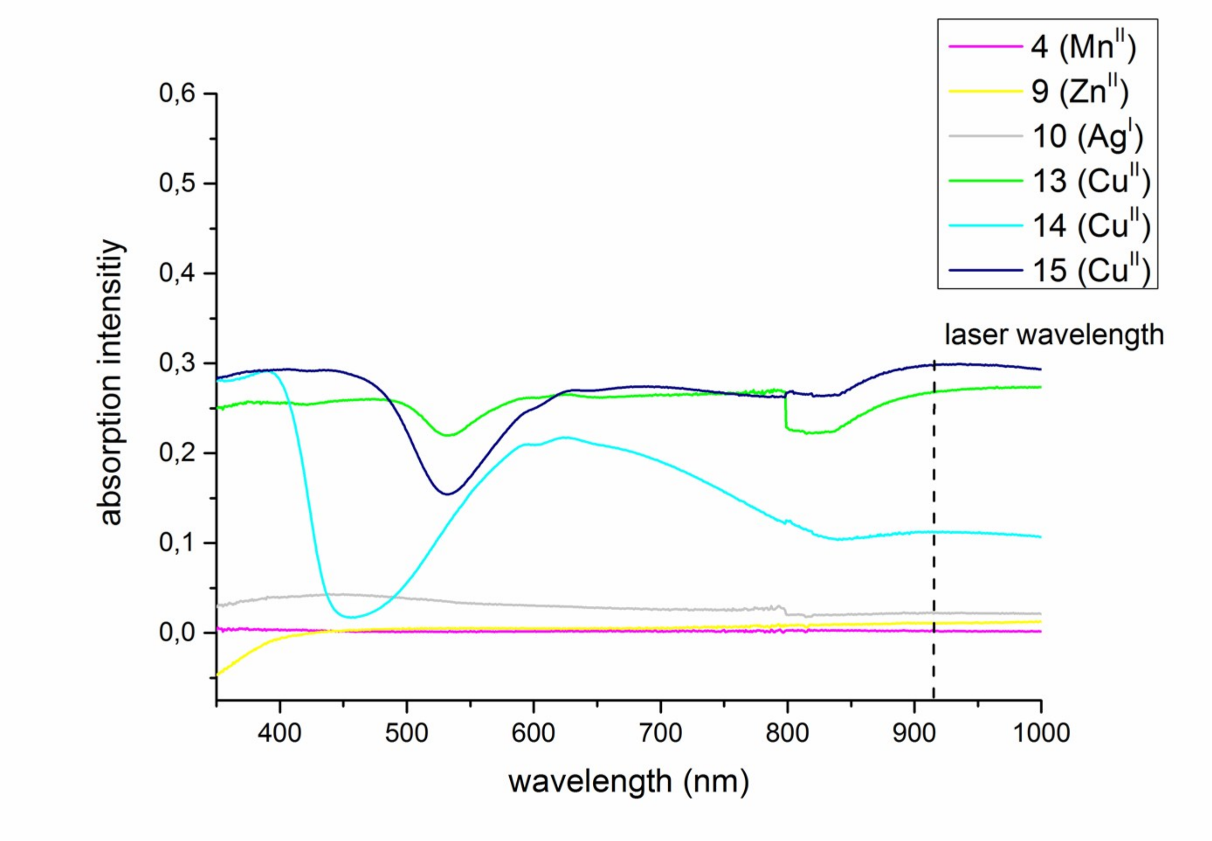


Figure S23 UV-Vis spectra in the solid state of coordination compounds **4**, **9**, **10** and **13**–**15**.

9. Experimental part and general methods

All chemicals and solvents were employed as received (Sigma-Aldrich, Fluka, Acros, ABCR). ^{1}H, ^{13}C and ^{15}N NMR 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) and nitromethane (^{15}N) in d_6-DMSO or d_3-MeCN as the solvents. The ^{1}H,^{15}N-HMBC NMR spectrum was measured with a data matrix of 1024 x 256, an applied zero filling of 2048 x 4096, 32 scans per round, a relaxation delay of 1 second, an acquisition time of 0.3 second at a concentration of 140 mg/mL and an overall measurement time of approx. 3 h. 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 thermal gravimetric analysis (TGA) with a PerkinElmer TGA4000. 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 were 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). UV-Vis spectra were recorded in the solid state using a Varian Cary 500 spectrometer in the wavelength range of 350–1000 nm. The step in the absorption intensity at 800 nm is caused by a detector change. Impact sensitivity tests were carried out according to STANAG 4489[S9] with a modified instruction[S10] using a BAM (Bundesanstalt für Materialforschung) drophammer.[S11] Friction sensitivity tests were carried out according to STANAG 4487[S12] with a modified instruction[S13] using the BAM friction tester. The classification of the tested compounds results from the "UN Recommendations on the Transport of Dangerous Goods".[S14] Additionally all compounds were tested upon the sensitivity toward electrical discharge using the OZM Electric Spark Tester ESD 2010 EN or OZM Electric Spark XSpark10 device.[S15] 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 shows only 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. Liquid-dried luminescent bacteria of the strain Vibrio fischeri NRRL-B-11177 provided by the HACH LANGE GmbH were used for the luminescent bacteria inhibition test to determine their toxicity toward aquatic organisms according to a modified procedure.[S16] 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 (especially compounds* ***5, 6, 8, 9*** *and* ***10–13****) 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.*

Procedure for the preparation of the propyl-linked ditetrazoles (1–3):

Main Method A:

The synthesis of the desired ditetrazoles was carried out analogously to a modified literature procedure:[S17] 1,3-dibromopropane (14.0 g, 69.3 mmol, 7.07 mL), sodium hydroxide (5.54 g, 139 mmol), 1,5*H*-tetrazole (9.72 g, 139 mmol) and tetrabutyl ammoniumbromide (2.23 g, 6.93 mmol) as phase transfer catalyst were dissolved in a mix of toluene and water (30 mL each). The resulting reaction mixture was stirred for 20 h at 120 °C under reflux, cooled to room temperature and concentrated through evaporation of the solvent under reduced pressure. The crude was purified by column chromatography on silica using ethyl acetate/methanol mixtures (gradient: 0–10 % methanol) to yield 2.29 g (12.7 mmol, 18 %) 2,2-dtp (**3**) (0 % methanol, R_f 0.8) as a yellow oil, 5.13 g (28.5 mmol, 41 %) of 1,2-dtp (**2**) (0 % methanol, R_f 0.3) in form of colorless blocks and 1.46 g (8.10 mmol, 12 %) of 1,1-dtp (10 % methanol, R_f 0.3) as a colorless solid. After recrystallization of 1,3-di(tetrazol-1-

yl)propane from water, filtration and drying overnight, compound **1** could be isolated in the form of colorless crystals.

Main Method B:

Alternative preparation of the ditetrazoles was achieved through addition of 1,3-dibromopropane (7.27 g, 36.0 mmol) in acetone (40 mL) to a mixture of 1,5*H*-tetrazole (6.00 g, 85.6 mmol) and triethylamine (8.66 g, 85.6 mmol) in acetone (40 mL). The reaction mixture was refluxed for four hours at 60 °C until a clear solution was obtained, which turned cloudy afterwards. After cooling down to room temperature and filtration of the triethylammonium bromide precipitate, the solvent was removed under reduced pressure. Treatment of the resulting oil with dioxane (100 mL) led to isolation of residual $HNEt_3Br$, which was filtered off. The obtained filtrate was treated with ethanol (100 mL) resulting in the precipitation of 1,1-dtp. The ditetrazole **1** was received in a yield of 586 mg (3.25 mmol, 9 %) after filtration and recrystallization from water. The two remaining isomers could be purified by column chromatography on silica gel using ethyl acetate, yielding 1.57 g (8.71 mmol, 24 %) of **3** (R_f 0.8) and 2.13 g (11.8 mmol, 33 %) of **2** (R_f 0.4).

Secondary Method:

Synthesis of the propyl-linked ditetrazoles with sodium hydroxide as base in water without phase transfer catalyst was performed according to a modified literature procedure described by Bronisz *et al.*[S18]. 1,3-Dibromopropane (5.05 g, 25.0 mmol) was added dropwise over a time period of 30 min to a suspension of 1,5*H*-tetrazole (4.20 g, 59.9 mmol) and sodium hydroxide (2.40 g, 60.0 mmol) in water (20 mL). This mixture was stirred under reflux for 6 h at 110 °C, cooled to room temperature and extracted with chloroform (8 x 20 mL) and dichloromethane (2 x 20 mL). The aqueous phase was concentrated under reduced pressure and the residue extracted with boiling acetonitrile (200 mL). The solid material obtained after evaporation was washed with ethanol and recrystallized from water affording 279 mg (1.41 mmol, 6 %) of ditetrazole **1**. The combined organic phases (CH_3Cl and CH_2Cl_2) were dried over magnesium sulfate and the solvent removed. The oily residue was washed with ethanol yielding a second crop of **1** (120 mg, 0.60 mmol, 2 %), which was filtrated and dried in air overnight. The remaining two isomers were separated by column chromatography on silica gel with ethyl acetate as mobile phase yielding 134 mg (0.74 mmol, 3 %) of **3** (R_f 0.8) and 277 mg (1.54 mmol, 6 %) of **2** (R_f 0.4).

1,3-Di(tetrazol-1-yl)propane • H_2O (1)

DTA (5 °C min^{-1}): 68 °C (endothermic), 126 °C (endothermic), 205 °C (exothermic); IR (ATR, cm^{-1}): = 3494 (w), 3481 (w), 3406 (m), 3317 (w), 3143 (w), 3130 (m), 3082 (m), 3007 (w), 2976 (w), 2938 (w), 1684 (m), 1495 (m), 1450 (m), 1433 (m), 1391 (w), 1373 (w), 1362 (w), 1281 (w), 1260 (w), 1244 (w), 1190 (m), 1173 (s), 1143 (m), 1112 (s), 1102 (vs), 1064 (m), 1031 (w), 993 (m), 976 (m), 924 (w), 894 (m), 874 (w), 803 (m), 744 (m), 722 (m), 681 (m), 666 (s), 647 (s), 625 (s);^{1}H NMR (DMSO-d_6, 25 °C, ppm) δ: 9.40 (s, 2H, -C*H*), 4.55 (t, 4H, -CH_2), 3.30 (s, 2H, H_2O), 2.50 (m, 2H, -CH_2); ^{13}C NMR (DMSO-d_6, 25 °C, ppm) δ: 144.1 (-CN_4), 44.8 (-CH_2), 29.0 (-CH_2); ^{1}H, ^{15}N HMBC NMR (MeCN-d_3, 25 °C, ppm) δ: 11.3 (N3), −14.3 (N2), −52.6 (N4, $^2J_{N\text{-}H}$ = 12 Hz), −145.1 (N1, $^2J_{N\text{-}H}$ = 8 Hz); EA: ($C_5H_{10}N_8O$, 198.19) calcd: C 30.30, H 5.09, N 56.84 %; found: C 30.80, H 4.92, N 56.78 %; BAM drophammer: > 40 J; friction tester: > 360 N; ESD: 1.35 J (at grain size < 100 μm).

1-(Tetrazol-1-yl)-3-(tetrazol-2-yl)propane (2)

DTA (5 °C min^{-1}): 50 °C (endothermic), 212 °C (exothermic); IR (ATR, cm^{-1}): = 3115 (s), 3003 (w), 2966 (w), 1821 (w), 1792 (w), 1484 (m), 1454 (s), 1442 (s), 1428 (w), 1391 (w), 1364 (m), 1356 (m), 1328 (w), 1290 (s), 1260 (w), 1243 (w), 1192 (m), 1165 (vs), 1142 (vs), 1107 (vs), 1077 (m), 1038 (m), 1031 (s), 1019 (w), 1010 (s), 981 (s), 964 (s), 912 (m), 898 (s), 871 (m), 826 (m), 720 (w), 706 (s), 683 (w), 660 (vs), 635 (s); ^{1}H NMR (DMSO-d_6, 25 °C, ppm) δ: 9.38 (s, 1H, -C*H*), 8.96 (s, 1H, -C*H*), 4.80 (t, 2H, -CH_2), 4.56 (t, 2H, -CH_2), 2.57 (pseudo quintet, 2H, -CH_2); ^{13}C NMR (DMSO-d_6, 25 °C, ppm) δ: 153.3 (-*C*N$_4$), 144.0 (-*C*N$_4$), 49.7 (-*C*H$_2$), 44.8 (-*C*H$_2$), 28.3 (-*C*H$_2$); ^{15}N NMR (MeCN-d_3, 25 °C, ppm) δ: 11.3 (N3, d, $^{3}J_{N\text{-}H}$ = 3.1 Hz), −3.3 (N7), −14.3 (N2), −49.0 (N8, d, $^{2}J_{N\text{-}H}$ = 13.4 Hz), −52.6 (N4), −77.3 (N5, d, $^{2}J_{N\text{-}H}$ = 14.5 Hz), −96.7 (N6, m), −145.1 (N1, m); EA: ($C_5H_8N_8$, 180.18) calcd: C 33.33, H 4.48, N 62.19 %; found: C 33.31, H 4.48, N 62.05 %; BAM drophammer: > 40 J; friction tester: > 360 N; ESD: 1.50 J (at grain size < 100 µm).

1,3-Di(tetrazol-2-yl)propane (3)

Ditetrazole **3** could be solidified through controlled freezing with liquid nitrogen and subsequent thawing to room temperature where the compound has been obtained in the form of colorless single crystal blocks suitable for X-ray diffraction.

DTA (5 °C min^{-1}): 45 °C (endothermic), 246 °C (exothermic); IR (ATR, cm^{-1}): = 3142 (w), 2964 (vw), 1628 (vw), 1574 (vw), 1448 (m), 1361 (m), 1283 (vs), 1185 (m), 1168 (w), 1134 (s), 1051 (w), 1026 (vs), 1008 (s), 986 (m), 883 (m), 826 (vw), 802 (w), 757 (vw), 728 (vw), 708 (s), 688 (s), 660 (w), 639 (w); ^{1}H NMR (DMSO-d_6, 25 °C, ppm) δ: 8.96 (s, 2H, -C*H*), 4.82 (t, 4H, -CH_2), 2.63 (q, 2H, -CH_2); ^{13}C NMR (DMSO-d_6, 25 °C, ppm) δ: 153.3 (-*C*N$_4$), 49.6 (-*C*H$_2$), 28.1 (-*C*H$_2$), ^{15}N NMR (MeCN-d_3, 25 °C, ppm) δ: −3.0 (N3), −49.0 (N4, d, $^{2}J_{N\text{-}H}$ = 12.5 Hz), −77.0 (N1, dt, $^{2}J_{N\text{-}H}$ = 14.5 Hz,$^{3}J_{N\text{-}H}$ = 1.6 Hz), −96.0 (N2, m); EA: ($C_5H_8N_8$, 180.18) calcd: C 33.33, H 4.48, N 62.19 %; found: C 33.38, H 4.47, N 62.00 %; BAM drophammer: > 40 J; friction tester: > 360 N; ESD: 0.15 J (at grain size < 100 μm).

General procedure for the preparation of metal(II) (Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}) 1,1-dtp perchlorate complexes (4–9):

A solution of 1,3-di(tetrazol-1-yl)propane monohydrate (**1**, 178 mg, 0.90 mmol) in acetonitrile (2 mL) was added to the corresponding metal(II) perchlorate salt (**4**: manganese(II) perchlorate hexahydrate (109 mg, 0.30 mmol); **5**: iron(II) perchlorate hexahydrate (110 mg, 0.30 mmol); **6**: cobalt(II) perchlorate hexahydrate (110 mg, 0.30 mmol); **7**: nickel(II) perchlorate hexahydrate (110 mg, 0.30 mmol); **8**: copper(II) perchlorate hexahydrate (111 mg, 0.30 mmol); **9**: zinc(II) perchlorate hexahydrate (111 mg, 0.30 mmol)) dissolved in water (1 mL). The colored reaction mixtures were mechanically stirred for one minute at room temperature and left for crystallization. After precipitation of a solid material, the compounds were filtered off, washed and dried in air.

[Mn(1,1-dtp)$_3$](ClO$_4$)$_2$ (4)

Within two hours, the manganese(II) complex **4** was obtained in the form of colorless blocks suitable for X-ray determination from the mother liquor. Yield: 183 mg (0.23 mmol, 77 %).

DTA (5 °C min^{-1}): 243 °C (exothermic); IR (ATR, cm^{-1}): = 3136 (w), 1503 (m), 1445 (w), 1430 (w), 1377 (vw), 1176 (m), 1091 (vs), 1085 (vs), 987 (m), 890 (w), 871 (w), 695 (w), 647 (m), 623 (s); UV-Vis spectrum: λ_{max} = none; EA: ($C_{15}H_{24}Cl_2MnN_{24}O_8$, 794.36): calcd: C 22.68, H 3.05, N 42.32 %; found: C 22.90, H 3.15, N 42.04 %; BAM drophammer: 3 J; friction tester: 216 N; ESD: 0.30 J (at grain size < 100 μm).

$[Fe(1,1\text{-}dtp)_3](ClO_4)_2$ (5)

After one hour compound **5** was received in form of X-ray suitable yellow blocks. Yield: 191 mg (0.24 mmol, 80 %).

DTA (5 °C min^{-1}): 234 °C (exothermic); IR (ATR, cm^{-1}): = 3139 (w), 1505 (m), 1447 (w), 1431 (w), 1377 (w), 1290 (vw), 1177 (m), 1144 (w), 1084 (vs), 990 (m), 936 (vw), 890 (w), 871 (w), 696 (w), 666 (vw), 647 (m), 623 (s); UV-Vis spectrum: λ_{max} = 893 nm; EA: ($C_{15}H_{24}Cl_2FeN_{24}O_8$, 795.26): calcd: C 22.65, H 3.04, N 42.27 %; found: C 22.92, H 3.06, N 42.15 %; BAM drophammer: 2 J; friction tester: 72 N; ESD: 0.10 J (at grain size < 100 µm).

$[Co(1,1\text{-}dtp)_3](ClO_4)_2$ (6)

Overnight, cobalt(II) complex **6** was obtained in the form of orange crystals suitable for X-ray determination. Yield: 125 mg (0.16 mmol, 53 %).

DTA (5 °C min^{-1}): 255 °C (exothermic); IR (ATR, cm^{-1}): = 3140 (w), 1505 (m), 1448 (w), 1431 (w), 1377 (vw), 1290 (vw), 1177 (m), 1144 (vw), 1084 (vs), 993 (m), 964 (w), 890 (w), 870 (w), 720 (vw), 697 (w), 665 (vw), 646 (m), 623 (s); UV-Vis spectrum: λ_{max} = 468, 982 nm; EA: ($C_{15}H_{24}Cl_2CoN_{24}O_8$, 798.35): calcd: C 22.57, H 3.03, N 42.11 %; found: C 22.83, H 3.17, N 42.11 %; BAM drophammer: 1 J; friction tester: 18 N; ESD: 0.08 J (at grain size < 100 µm).

$[Ni(1,1\text{-}dtp)_3](ClO_4)_2$ (7)

After addition of the nickel(II) salt a cloudy lilac solution was formed. Within one hour complex **7** was isolated in the form of a purple amorphous solid. Yield: 200 mg (0.25 mmol, 84 %).

DTA (5 °C min^{-1}): 297 °C (exothermic); IR (ATR, cm^{-1}): = 3143 (w), 1506 (m), 1450 (w), 1432 (w), 1378 (w), 1179 (m), 1085 (vs), 996 (m), 964 (w), 889 (w), 871 (w), 697 (w), 647 (m), 623 (s); UV-Vis spectrum: λ_{max} = 547, 891 nm; EA: ($C_{15}H_{24}Cl_2N_{24}NiO_8$, 798.11): calcd: C 22.57, H 3.03, N 42.12 %; found: C 22.67, H 3.05, N 42.01 %; BAM drophammer: 3 J; friction tester: 120 N; ESD: 0.20 J (at grain size < 100 µm).

[Cu(1,1-dtp)$_3$](ClO$_4$)$_2$ (8)

Overnight, blue single crystal blocks of copper(II) complex **8** suitable for X-ray determination were received. Yield: 96.4 mg (0.12 mmol, 40 %).

DTA (5 °C min^{-1}): 231 °C (exothermic); IR (ATR, cm^{-1}): = 3141 (w), 1506 (w), 1449 (w), 1431 (w), 1177 (m), 1085 (vs), 1001 (m), 986 (m), 964 (w), 889 (w), 871 (w), 696 (w), 646 (m), 623 (s); UV-Vis spectrum: λ_{max} = 701 nm; EA: ($C_{15}H_{24}Cl_2CuN_{24}O_8$, 802.96): calcd: C 22.44, H 3.01, N 41.87 %; found: C 22.51, H 3.03, N 41.71 %; BAM drophammer: 1 J; friction tester: 54 N; ESD: 0.33 J (at grain size < 100 µm).

[Zn(1,1-dtp)$_3$](ClO$_4$)$_2$ (9)

Coordination compound **9** was received within two hours in the form of colorless blocks suitable for X-ray determination. Yield: 193 mg (0.24 mmol, 80 %).

DTA (5 °C min^{-1}): 253 °C (exothermic); IR (ATR, cm^{-1}): = 3139 (w), 1505 (w), 1448 (w), 1431 (w), 1177 (w), 1091 (vs), 1085 (vs), 993 (m), 963 (w), 892 (w), 871 (w), 696 (w), 647 (m), 624 (s); UV-Vis spectrum: λ_{max} = none; EA: ($C_{15}H_{24}Cl_2N_{24}O_8Zn$, 804.80): calcd: C 22.39, H 3.01, N 41.77 %; found: C 22.50, H 2.99 , N 41.75 %; BAM drophammer: 1 J; friction tester: 288 N; ESD: 0.20 J (at grain size < 100 μm).

[Ag(1,2-dtp)]ClO_4 (10)

An aqueous solution (10 mL) of 1-(tetrazol-1-yl)-3-(tetrazol-2-yl)propane (**2**, 27.1 mg, 0.25 mmol) was heated to 70 °C and treated with silver(I) perchlorate (52.0 mg, 0.25 mmol), dissolved in water (10 mL). The reaction mixture was mechanically stirred for one minute and afterwards left to crystallize at room temperature. Silver(I) complex **10** crystallized within one day in the form of colorless blocks suitable for X-ray determination. The crystals were filtered off, washed with cold ethanol (2 mL) and dried in air. Yield: 55.0 mg (0.14 mmol, 57 %).

DTA (5 °C min^{-1}): 185 °C (exothermic); IR (ATR, cm^{-1}): = 3169 (w), 3120 (m), 3030 (vw), 3010 (vw), 2974 (vw), 2965 (vw), 1782 (vw), 1493 (w), 1467 (w), 1444 (w), 1435 (w), 1426 (w), 1373 (w), 1356 (w), 1349 (w), 1337 (vw), 1309 (w), 1284 (w), 1195 (m), 1153 (m), 1125 (m), 1071 (vs), 1047 (vs), 1018 (m), 998 (m), 982 (s), 934 (w), 888 (m), 871 (m), 824 (m), 729 (vw), 716 (w), 696 (m), 686 (w), 660 (m), 636 (w), 618 (vs); UV-Vis spectrum: λ_{max} = none; EA: ($C_5H_8AgClN_8O_4$, 387.49): calcd: C 15.50, H 2.08, N 28.92 %; found: C 15.73, H 2.45 , N 28.25 %; BAM drophammer: 8 J; friction tester: 16 N; ESD: 0.15 J (at grain size < 100 μm).

[Cu(1,2-dtp)$_3$](ClO_4)$_2$ (11)

The ditetrazole ligand 1,2-dtp (135 mg, 0.75 mmol) was dissolved in distilled water (4 mL), heated to 70 °C and added to an aqueous solution (1 mL) of copper(II) perchlorate hexahydrate (93.0 mg, 0.25 mmol). After mechanically stirring for one minute at room temperature, the reaction mixture was left for crystallization. X-ray suitable single crystals of complex **11** were obtained after 5 days. The blue rods were filtered off, washed with cold ethanol (2 mL) and dried in air. Yield: 179 mg (0.22 mmol, 89 %).

DTA (5 °C min^{-1}): 222 °C (exothermic); IR (ATR, cm^{-1}): = 3136 (w), 1504 (w), 1445 (w), 1366 (w), 1309 (w), 1179 (w), 1145 (w), 1082 (vs), 1022 (m), 1006 (m), 988 (w), 962 (w), 933 (w), 890 (w), 872 (w), 701 (w), 680 (w), 665 (w), 657 (w), 622 (s); UV-Vis spectrum: λ_{max} = 688 nm; EA: ($C_{15}H_{24}Cl_2CuN_{24}O_8$, 802.96): calcd: C 22.44, H 3.01, N 41.87 %; found: C 22.28, H 2.98 , N 41.80 %; BAM drophammer: 1.5 J; friction tester: 18 N; ESD: 0.10 J (at grain size < 100 μm).

$[Cu(H_2O)_2(2,2\text{-dtp})_2](ClO_4)_2$ (12)

1,3-Di(tetrazol-2-yl)propane (**3**, 184 mg, 1.00 mmol) in acetonitrile (2 mL) was reacted with copper(II) perchlorate hexahydrate (185 mg, 0.50 mmol) dissolved in water (1 mL). The colored reaction mixture was stirred mechanically for one minute at room temperature and left for crystallization. After filtration of the product, the compound was washed with ethanol (2 mL) and dried in air. The diaqua complex **12** was received in form of blue block suitable for X-ray diffraction within one hour. Yield: 213 mg (0.32 mmol, 64 %).

DTA (5 °C min^{-1}): 132 °C (endothermic), 257 °C (exothermic); IR (ATR, cm^{-1}): =3569 (w), 3450 (w), 3347 (vw), 3156 (w), 3143 (w), 1629 (w), 1475 (vw), 1464 (w), 1454 (w), 1391 (w), 1370 (w), 1311 (w), 1207 (w), 1199 (w), 1152 (m), 1097 (vs), 1064 (vs), 1047 (vs), 1033 (s), 1020 (s), 931 (w), 897 (m), 807 (w), 765 (w), 720 (w), 703 (m), 683 (m), 622 (vs); UV-Vis spectrum: λ_{max} = 654 nm; EA: ($C_{10}H_{20}Cl_2CuN_{16}O_{10}$, 658.82): calcd: C 18.23, H 3.06, N 34.02 %; found: C 18.31, H 3.07 , N 34.02 %; BAM drophammer: 1.5 J friction tester: 64 N; ESD: 0.30 J (at grain size < 100 µm).

[Cu(TNR)(1,1-dtp)] · H_2O (13)

Styphnic acid (147 mg, 0.60 mmol) and copper(II) carbonate (37.0 mg, 0.30 mmol) were stirred in water (5 mL) at 70 °C until a clear solution was obtained. An aqueous solution of 1,3-di(tetrazol-1-yl)propane monohydrate (**1,** 59.5 mg, 0.30 mmol) was added, which was afterwards further stirred mechanically for five minutes. The reaction mixture was left for crystallization at room temperature until a solid appeared. The resulting product was filtered off, washed with a small amount of cold ethanol (2 mL) and dried in air. The copper(II) complex **13** was obtained in the form of green crystals suitable for X-ray determination after a few minutes. Yield: 119 mg (0.24 mmol, 80 %).

DTA (5 °C min^{-1}): 88 °C (endothermic), 248 °C (exothermic); IR (ATR, cm^{-1}): = 3662 (w), 3634 (w), 3574 (w), 3134 (w), 3018 (w), 2971 (w), 1606 (m), 1581 (m), 1521 (s), 1495 (s), 1478 (m), 1436 (s), 1374 (m), 1353 (m), 1289 (s), 1232 (vs), 1175 (vs), 1140 (s), 1098 (vs), 1013 (s), 953 (m), 926 (m), 916 (m), 890 (m), 847 (m), 827 (w), 792 (m), 768 (m), 759 (m), 738 (m), 706 (vs), 677 (s), 652 (s), 623 (m); UV-Vis spectrum: λ_{max} = 390, 696 nm; EA: ($C_{11}H_{11}CuN_{11}O_9$, 504.83): calcd: C 26.17, H 2.20, N 30.52 %; found: C 26.56, H 2.32 , N 30.17 %; BAM drophammer: 10 J; friction tester: > 360 N; ESD: 0.50 J (at grain size < 100 µm).

[Cu(H_2O)$_2$(1,1-dtp)$_2$](CDNM)$_2$ (14)

Potassium cyanodinitromethanide (102 mg, 0.60 mmol) and copper(II) sulfate pentahydrate (75.0 mg, 0.30 mmol) were dissolved in water (3 mL), heated to 70 °C and stirred for three minutes. The nitrogen-rich ditetrazole **1** (119 mg, 0.60 mmol) dissolved in water (2 mL) was added, the whole reaction mixture further mechanically stirred for three more minutes and finally left for crystallization. From the mother liquor, blue single crystals suitable for X-ray determination of **14** could be obtained within two hours. Yield: 76.0 mg (0.11 mmol, 35 %).

DTA (5 °C min^{-1}): 93 °C (endothermic), 212 °C (exothermic); IR (ATR, cm^{-1}): = 3528 (m), 3435 (w), 3242 (w), 3180 (w), 3138 (m), 3048 (w), 3003 (w), 2223 (w), 2216 (w), 1629 (w), 1504 (s), 1491 (s), 1450 (m), 1438 (m), 1410 (m), 1393 (w), 1360 (w), 1341 (w), 1231 (vs), 1177 (s), 1149 (s), 1144 (s), 1107 (s), 1099 (s), 1082 (s), 1070 (m), 1062 (m), 1038 (m), 1009 (s), 882 (m), 847 (m), 791 (w), 766 (m), 746 (s), 717 (m), 675 (m), 654 (s), 611 (m); UV-Vis spectrum: λ_{max} = 389, 624 nm; EA: ($C_{14}H_{20}CuN_{22}O_{10}$, 720.03): calcd: C 23.35, H 2.80, N 42.80 %; found: C 23.49, H 2.75, N 42.81 %; BAM drophammer: 10 J; friction tester: > 360 N; ESD: 0.50 J (at grain size < 100 µm).

[Cu(1,1-dtp)$_3$](DN)$_2$ (15)

Ammonium dinitramide (80.0 mg, 0.60 mmol) and copper(II) sulfate pentahydrate (75.0 mg, 0.30 mmol) were mechanically mixed at 70 °C in water (3 mL). To this blue solution, ligand **1 (**178 mg, 0.90 mmol) dissolved in water (2 mL) was added and the whole reaction mixture stirred for three minutes. After two hours, dinitramide complex **15** could be isolated in the form of blue platelets suitable for X-ray determination. Yield: 202 mg (0.25 mmol, 83 %).

DTA (5 °C min^{-1}): 153 °C (exothermic); IR (ATR, cm^{-1}): = 3137 (w), 3015 (vw), 2968 (vw), 1509 (m), 1438 (m), 1420 (m), 1336 (w), 1298 (w), 1178 (vs), 1167 (vs), 1102 (s), 1069 (m), 1001 (s), 975 (s), 887 (m), 825 (m), 789 (m), 754 (s), 718 (m), 679 (w), 657 (s), 618 (w); UV-

Vis spectrum: λ_{max} = 377, 630 nm; EA: ($C_{15}H_{24}CuN_{30}O_8$, 816.12): calcd: C 22.08, H 2.96, N 51.49 %; found: C 22.19, H 2.88 , N 51.32 %; BAM drophammer: 3 J; friction tester: > 360 N; ESD: 0.70 J (at grain size < 100 µm).

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S14 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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