Supplementary Information

Tailoring the properties of 3d transition metal complexes with different *N*-cycloalkyl-substituted tetrazoles

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1. IR spectroscopy

Fig. S1 Infrared spectra of ligands **1**–**3** and copper(II) nitrate complexes **5**–**7**.
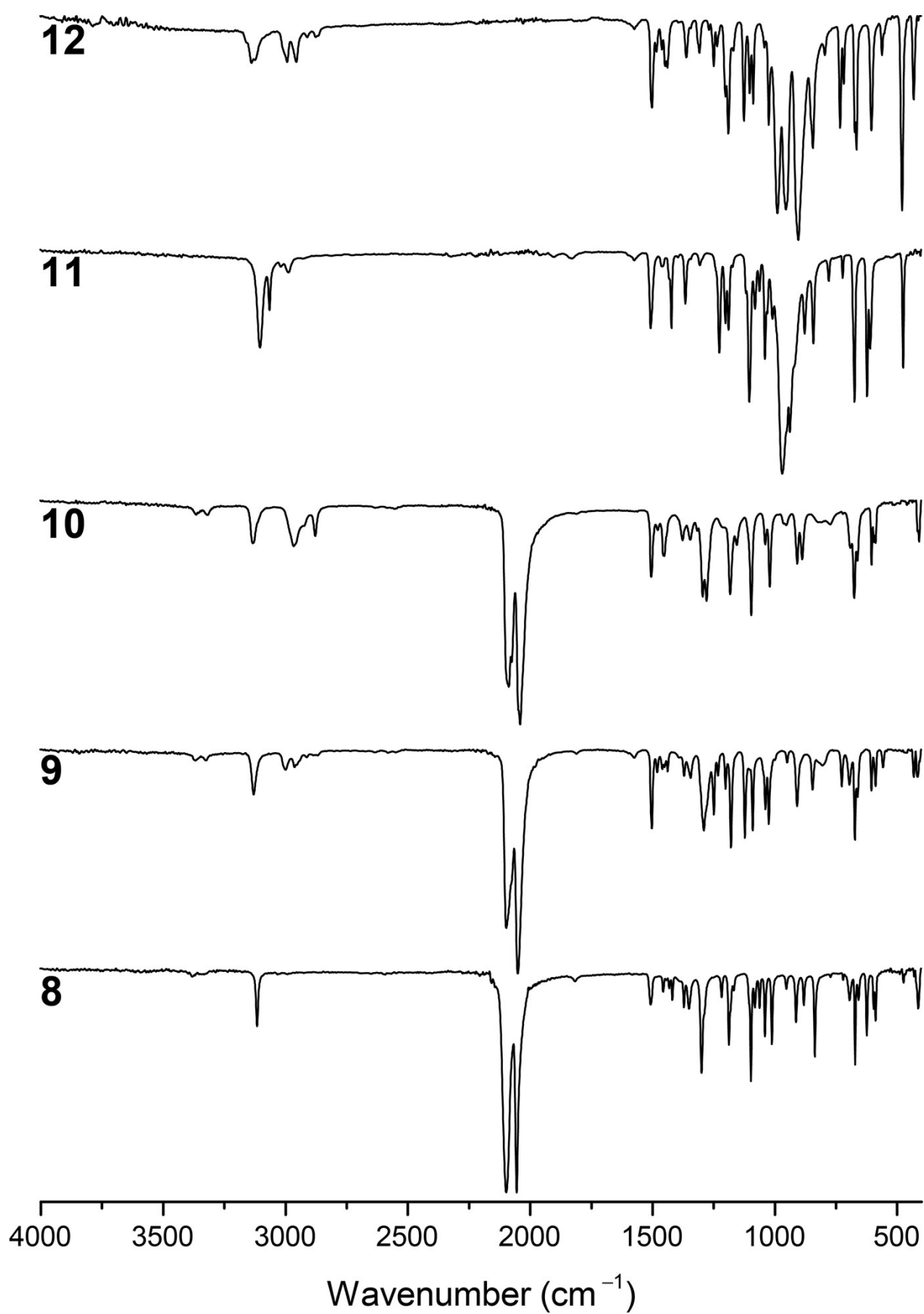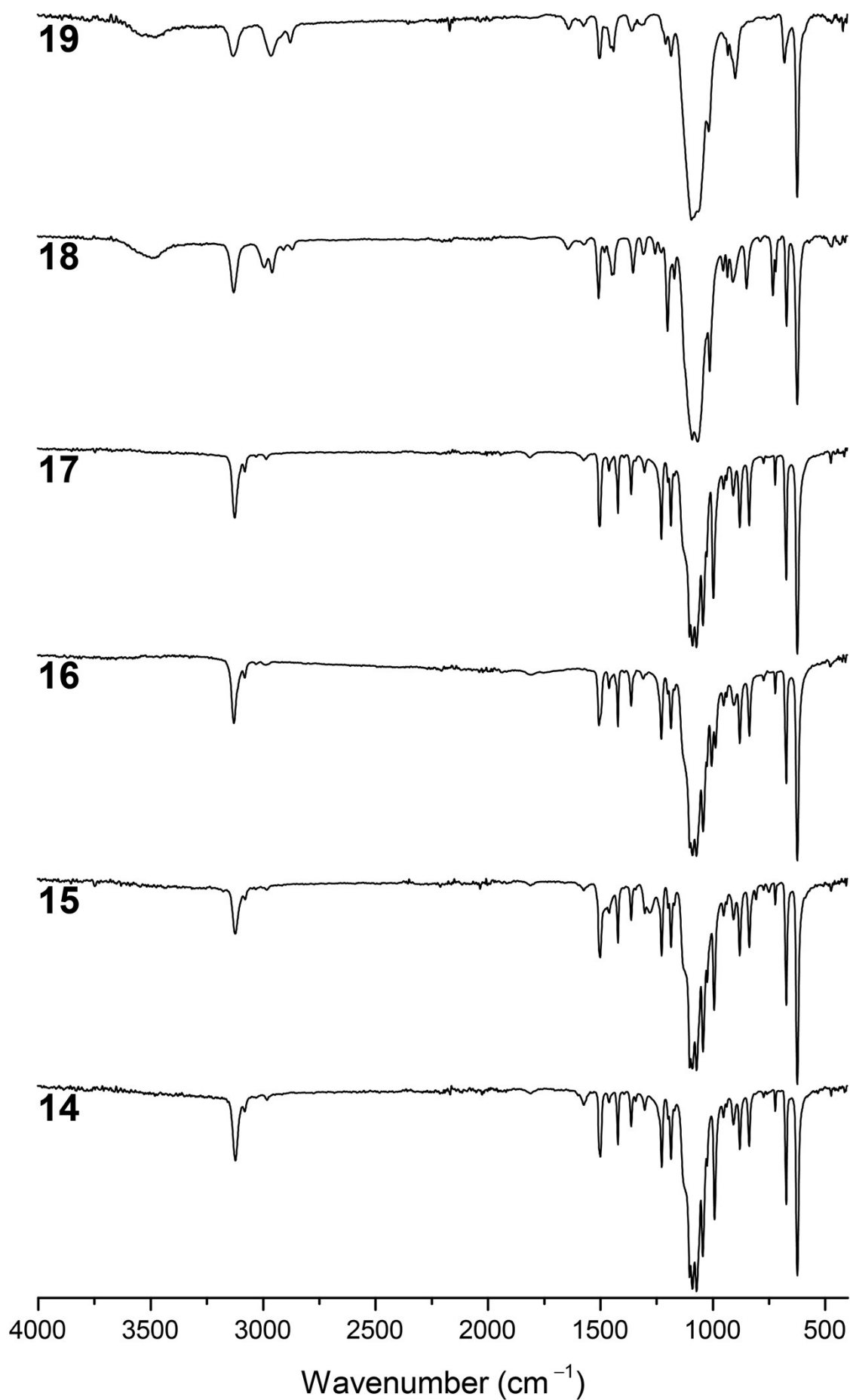
Fig. S2   IR spectra of ECC **8**–**12**.

Fig. S3 Infrared spectra of perchlorate compounds **14–19**.

2. ¹H-¹⁵N-HMBC NMR spectroscopy
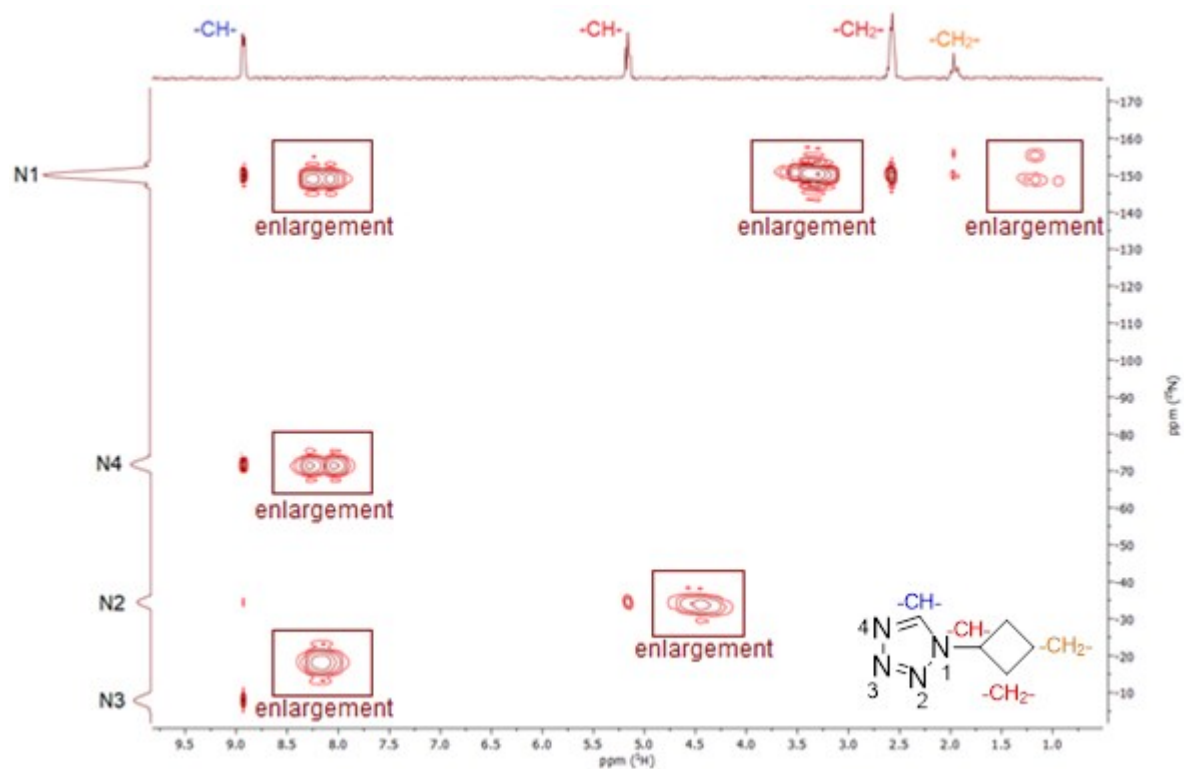
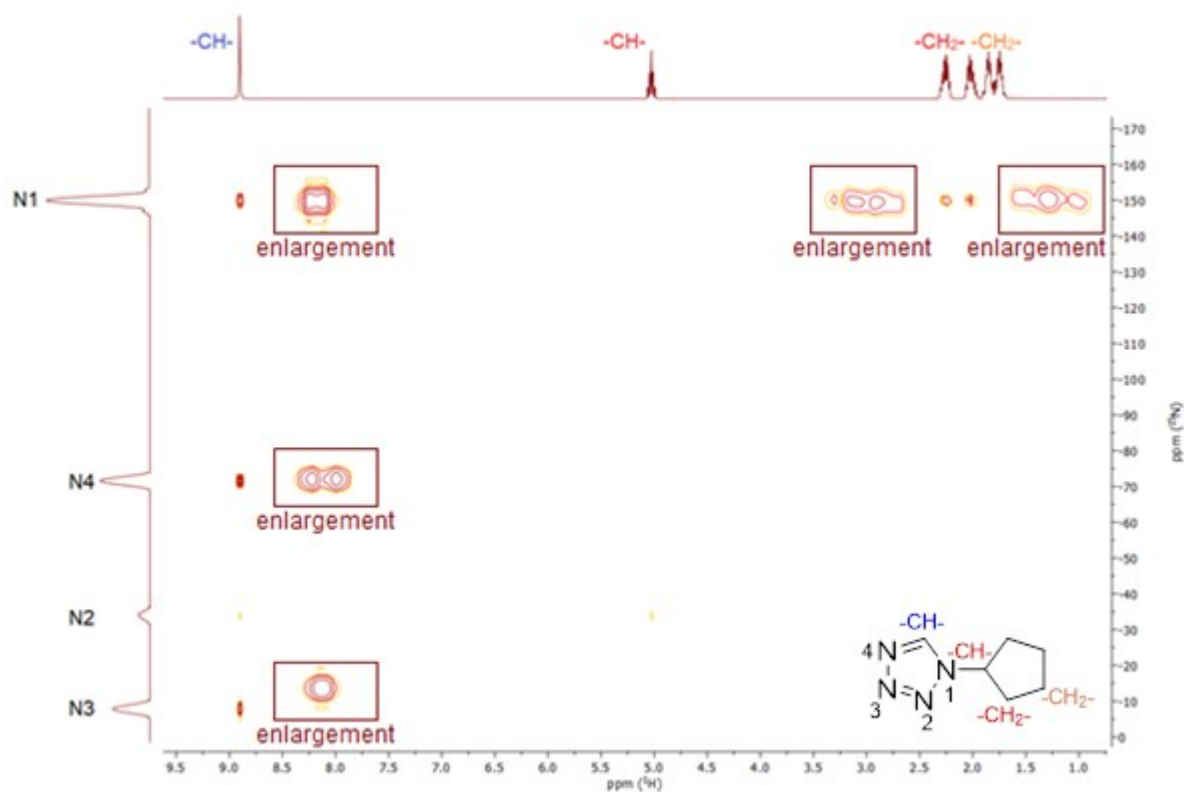**Fig. S4** ¹H-¹⁵N-HMBC NMR spectrum of ligand C₄tz (**2**).

Fig. S5 ¹H-¹⁵N-HMBC NMR spectrum of ligand C₅tz (**3**).

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-$K\alpha$ radiation ($\lambda = 0.7107$ 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 $F2$ (SHELXL[S4]) and finally checked using the PLATON software[S5] integrated in the WinGX[S6] software suite. The non-hydrogen atoms were refined anisotropically. 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**, and **4–6**.

	1	**4**	**5**	**6**
Formula	$C_4H_6N_4$	$C_{16}H_{24}Cu_2N_{20}O_{12}$	$C_{32}H_{52}Cu_2N_{36}O_{14}$	$C_{15}H_{24}CuN_{14}O_6$
FW [g mol^{-1}]	110.13	815.63	1292.17	560.02
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic
Space Group	$P2_1$	$Pna2_1$	$P–1$	Ia
Colour / Habit	colourless platelet	blue block	blue block	blue block
Size [mm]	0.14 x 0.49 x 0.50	0.11 x 0.13 x 0.29	0.25 x 0.30 x 0.50	0.20 x 0.30 x 0.39
a [Å]	4.9091(9)	19.4982(5)	11.2105(7)	10.4489(4)
b [Å]	6.6220(8)	15.0587(5)	11.3324(8)	13.0298(5)
c [Å]	8.103(2)	20.7916(5)	11.4691(7)	17.6353(7)
α [°]	90	90	104.328(6)	90
β [°]	99.75(2)	90	106.897(5)	102.235(4)
γ [°]	90	90	91.541(5)	90
V [Å^3]	259.61(9)	6104.8(3)	1343.09(16)	2346.46(16)
Z	2	8	1	4
$\rho_{calc.}$ [g cm^{-3}]	1.409	1.775	1.598	1.585
μ [mm^{-1}]	0.099	1.486	0.888	0.995
$F(000)$	116	3312	666	1156
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	112	110	113	105
θ Min–Max [°]	4.0, 30.5	2.5, 32.3	1.9, 26.4	2.0, 30.5
Dataset	−6: 6; −9: 9; −11: 9	−29: 29; −21: 21; −30: 24	−13: 14; −13: 14; −11: 14	−14: 14; −18: 18; −25: 25
Reflections collected	2494	56214	7859	23149
Independent refl.	1571	18817	5412	7161
R_{int}	0.024	0.086	0.024	0.033
Observed reflections	1319	12571	4547	6720
Parameters	97	902	483	422
R_1 (obs)[a]	0.0434	0.0590	0.0359	0.0269
wR_2 (all data)[b]	0.0941	0.1121	0.0880	0.0604
GooF[c]	1.10	1.02	1.03	1.06
Resd. Dens. [e Å^{-3}]	−0.21, 0.21	−0.50, 0.77	−0.35, 0.34	−0.33, 0.42
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan
CCDC	2061069	2061078	2061087	2061071

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 **7–10**.

	7	8	9	10
Formula	$C_{12}H_{20}CuN_{10}O_6$	$C_4H_6CuN_{10}$	$C_5H_8CuN_{10}$	$C_{12}H_{20}Cu_2N_{20}$
FW [g mol^{-1}]	463.92	257.73	271.75	571.56
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space Group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Colour / Habit	blue plate	brown block	brown platelet	brown plate
Size [mm]	0.06 x 0.32 x 0.50	0.03 x 0.03 x 0.04	0.02 x 0.24 x 0.40	0.02 x 0.10 x 0.30
a [Å]	14.4782(13)	5.5870(3)	15.1598(14)	6.2935(15)
b [Å]	6.3738(3)	6.9121(4)	6.2457(3)	10.817(2)
c [Å]	9.7644(5)	13.0900(7)	10.8574(5)	16.387(3)
α [°]	90	96.426(2)	90	75.106(16)
β [°]	92.052(6)	99.436(2)	102.305(6)	82.860(18)
γ [°]	90	110.441(2)	90	89.884(17)
V [Å^3]	900.49(10)	459.38(4)	1004.40(12)	1069.2(4)
Z	2	2	4	2
$\rho_{calc.}$ [g cm^{-3}]	1.711	1.863	1.797	1.775
μ [mm^{-1}]	1.271	2.362	2.166	2.039
$F(000)$	478	258	548	580
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	105	102	106	112
θ Min–Max [°]	2.8, 26.4	3.2, 26.4	2.8, 26.4	2.6, 26.4
Dataset	−17: 18; −5: 7; −12: 11	−6: 6; −8: 8; −16: 16	−18: 18; −7: 7; −13: 13	−7: 7; −12: 13; −15: 20
Reflections collected	4777	9544	6720	6103
Independent refl.	1833	1867	2055	4320
R_{int}	0.054	0.037	0.056	0.064
Observed reflections	1429	1760	1547	2317
Parameters	173	160	145	307
R_1 (obs)^a	0.0506	0.0190	0.0450	0.0778
wR_2 (all data)^b	0.1371	0.0470	0.1066	0.1643
GooF^c	1.05	1.04	1.06	0.99
Resd. Dens. [e Å^{-3}]	−0.84, 1.26	−0.30, 0.39	−0.55, 1.46	−0.70, 1.46
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan
CCDC	2061075	2061086	2061084	2061085

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 **11–14**.

	11	12	13	14
Formula	$C_{24}H_{36}Cl_2CuN_{24}O_6$	$C_{20}H_{32}Cl_2CuN_{16}O_6$	$C_{24}H_{40}Cl_2CuN_{16}O_6$	$C_{24}H_{36}Cl_2MnN_{24}O_8$
FW [g mol^{-1}]	891.21	727.05	783.16	914.61
Crystal system	trigonal	monoclinic	monoclinic	trigonal
Space Group	*R*–3	*P*2$_1$/*c*	*I*2/*a*	*R*–3
Colour / Habit	blue platelet	blue plate	blue block	colourless plate
Size [mm]	0.11 x 0.24 x 0.27	0.15 x 0.41 x 0.76	0.22 x 0.54 x 0.56	0.14 x 0.59 x 0.64
a [Å]	10.9182(10)	6.7946(4)	21.6878(12)	10.8880(6)
b [Å]	10.9182(10)	18.1424(12)	6.4701(5)	10.8880(6)
c [Å]	28.166(3)	12.4720(7)	24.9341(13)	29.5174(17)
α [°]	90	90	90	90
β [°]	90	96.844(6)	104.209(4)	90
γ [°]	120	90	90	120
V [Å^3]	2907.8(7)	1526.47(16)	3391.8(4)	3030.4(4)
Z	3	2	4	3
$\rho_{calc.}$ [g cm^{-3}]	1.527	1.582	1.534	1.503
μ [mm^{-1}]	0.774	0.956	0.866	0.535
F(000)	1377	750	1628	1413
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	127	100	127	106
θ Min–Max [°]	2.3, 26.3	2.0, 26.4	2.2, 26.4	2.1, 26.3
Dataset	−13: 7; −12: 13; −35: 35	−8: 8; −22: 22; −15: 15	−26: 27; −8: 8; −30: 31	−13: 13; −12: 11; −13: 36
Reflections collected	7265	10086	14134	2261
Independent refl.	1328	3135	3468	1385
R_{int}	0.037	0.035	0.034	0.015
Observed reflections	1148	2587	3120	1240
Parameters	111	269	223	114
R_1 (obs)[a]	0.0299	0.0325	0.0304	0.0293
wR_2 (all data)[b]	0.0797	0.0774	0.0794	0.0768
GooF[c]	1.06	1.01	1.06	1.08
Resd. Dens. [e Å^{-3}]	−0.25, 0.32	−0.29, 0.38	−0.29, 0.34	−0.32, 0.33
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan
CCDC	2061081	2061079	2061076	2061073

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 S4   Crystallographic data of **15a**, **15b**, and **16**.

	15a	15b	16
Formula	$C_{24}H_{36}Cl_2FeN_{24}O_8$	$C_{24}H_{36}Cl_2FeN_{24}O_8$	$C_{24}H_{36}Cl_2CuN_{24}O_8$
FW [g mol^{-1}]	915.52	915.52	923.21
Crystal system	trigonal	trigonal	trigonal
Space Group	R–3	R–3	R–3
Colour / Habit	violet block	colourless block	blue hexagon
Size [mm]	0.15 x 0.20 x 0.22	0.20 x 0.20 x 0.20	0.05 x 0.37 x 0.46
a [Å]	10.7309(7)	10.8393(1)	10.7417(15)
b [Å]	10.7309(7)	10.8393(1)	10.7417(15)
c [Å]	29.207(2)	30.1945(6)	29.826(5)
α [°]	90	90	90
β [°]	90	90	90
γ [°]	120	120	120
V [Å^3]	2912.7(5)	3072.28(10)	2980.4(11)
Z	3	3	3
$\rho_{calc.}$ [g cm^{-3}]	1.566	1.485	1.543
μ [mm^{-1}]	0.605	0.574	0.761
$F(000)$	1416	1416	1425
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	107	297	115
θ Min–Max [°]	2.3, 26.4	2.6, 26.3	2.0, 26.4
Dataset	−13: 12; −13: 13; −36: 36	−13: 13; −13: 13; −37: 37	−13: 13; −13: 13; −33: 37
Reflections collected	5417	19341	7345
Independent refl.	1341	1401	1363
R_{int}	0.031	0.022	0.060
Observed reflections	1169	1328	1124
Parameters	114	107	90
R_1 (obs)[a]	0.0298	0.0662	0.0405
wR_2 (all data)[b]	0.0713	0.1712	0.0953
GooF[c]	1.05	1.16	1.06
Resd. Dens. [e Å^{-3}]	−0.32, 0.34	−0.67, 0.93	−0.25, 0.46
Absorption correction	multi-scan	multi-scan	multi-scan
CCDC	2061074	2061089	2061072

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 S5   Crystallographic data of **17–19**.

	17	18	19
Formula	$C_{24}H_{36}Cl_2N_{24}O_8Zn$	$C_{40}H_{68}Cl_4Cu_2N_{32}O_{18}$	$C_{48}H_{84}Cl_4Cu_2N_{32}O_{18}$
FW [g mol^{-1}]	925.04	1554.14	1666.35
Crystal system	trigonal	monoclinic	triclinic
Space Group	R–3	$P2_1/n$	P–1
Colour / Habit	colourless plate	blue block	blue block
Size [mm]	0.17 x 0.21 x 0.40	0.09 x 0.11 x 0.24	0.19 x 0.22 x 0.43
a [Å]	10.7815(5)	17.0836(7)	11.0187(5)
b [Å]	10.7815(5)	11.1197(5)	12.6481(8)
c [Å]	29.5910(18)	17.2721(9)	13.4478(8)
α [°]	90	90	86.257(5)
β [°]	90	93.681(4)	73.006(5)
γ [°]	120	90	82.596(5)
V [Å^3]	2978.9(4)	3274.3(3)	1776.63(18)
Z	3	2	1
$\rho_{calc.}$ [g cm^{-3}]	1.547	1.576	1.558
μ [mm^{-1}]	0.830	0.903	0.838
$F(000)$	1428	1604	866
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	107	111	103
θ Min–Max [°]	3.5, 26.4	2.2, 26.4	1.9, 32.3
Dataset	−11: 13; −13: 13; −33: 36	−17: 21; −13: 13; −18: 21	−14: 15; −17: 18; −20: 20
Reflections collected	6902	18424	20438
Independent refl.	1362	6677	11483
R_{int}	0.067	0.070	0.034
Observed reflections	1081	4331	8487
Parameters	114	472	617
R_1 (obs)[a]	0.0383	0.0579	0.0499
wR_2 (all data)[b]	0.0852	0.1217	0.1416
GooF[c]	1.01	1.01	1.07
Resd. Dens. [e Å^{-3}]	−0.31, 0.47	−0.40, 0.54	−0.52, 0.68
Absorption correction	multi-scan	multi-scan	multi-scan
CCDC	2061077	2061080	2061070

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 S6   Crystallographic data of **20–22**.

	20	21	22
Formula	$C_{24}H_{44}Cl_2MnN_{16}O_{10}$	$C_{24}H_{44}Cl_2FeN_{16}O_{10}$	$C_{24}H_{44}Cl_2ZnN_{16}O_{10}$
FW [g mol^{-1}]	842.59	842.49	853.02
Crystal system	triclinic	triclinic	triclinic
Space Group	$P–1$	$P–1$	$P–1$
Colour / Habit	colourless block	colourless block	colourless block
Size [mm]	0.30 x 0.40 x 0.40	0.15 x 0.40 x 0.40	0.12 x 0.30 x 0.35
a [Å]	10.7162(4)	10.9841(4)	10.9914(8)
b [Å]	11.9386(6)	11.8637(5)	11.9384(9)
c [Å]	15.5566(7)	15.0067(9)	14.9946(11)
α [°]	68.044(4)	112.565(5)	112.552(7)
β [°]	79.661(4)	90.518(4)	90.350(6)
γ [°]	77.005(4)	96.245(3)	96.674(6)
V [Å^3]	1788.58(15)	1792.38(16)	1802.1(3)
Z	2	1	2
$\rho_{calc.}$ [g cm^{-3}]	1.565	1.561	1.572
μ [mm^{-1}]	0.595	0.646	0.905
$F(000)$	878	878	888
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	106	109	101
θ Min–Max [°]	2.0, 28.3	1.9, 30.9	1.9, 26.4
Dataset	−8: 13; −15: 15; −19: 20	−15: 15; −16: 17; −20: 21	−13: 13; −14: 14; −18: 18
Reflections collected	12525	19528	16058
Independent refl.	7870	9842	7369
R_{int}	0.023	0.034	0.052
Observed reflections	6124	7128	5411
Parameters	497	518	493
R_1 (obs)[a]	0.0572	0.0623	0.0665
wR_2 (all data)[b]	0.1514	0.1709	0.1950
GooF[c]	1.03	1.04	1.04
Resd. Dens. [e Å^{-3}]	−0.92, 1.72	−0.72, 1.72	−1.02, 1.70
Absorption correction	multi-scan	multi-scan	multi-scan
CCDC	2061082	2061088	2061083

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 S7   Comparison of geometric parameters [Å, °] of **1** and cyclopropylamine.

1-cyclopropyl-5*H*-tetrazole	cyclopropylamine
N1–C2 1.448(3)	N1–C1 1.434
C2–C3 1.493(4),	C2–C3 1.490(3)
C2–C4 1.491(4),	C1–C3 1.489(4)
C3–C4 1.500(4)	C1–C2 1.500(3)
N1–C2–C3 117.8(2)	N1–C1–C2 116.2(2)
N1–C2–C4 118.5(2)	N1–C1–C3 117.0(2)
C3–C2–C4 60.36(19)	C3–C1–C2 60.48(15)
C2–C3–C4 59.76(18)	C1–C2–C3 59.75(16)
C2–C4–C3 59.89(19)	C1–C3–C2 59.78(15)
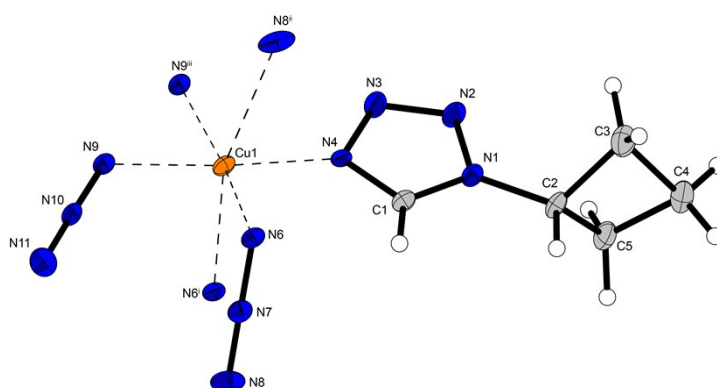
Fig. S6   Coordination environment around the copper(II) centre in **9**. Selected bond lengths (Å): Cu1–N4 1.983(3), Cu1–N6 2.003(3), Cu1–N9 2.002(3), Cu1–N6^{i} 2.520(3), Cu1–N8^{ii} 2.686(3); select bond angles (°): N4–Cu1–N6 90.63(13), N4–Cu1–N9 175.23(13), N4–Cu1–N6^{i} 87.47(12), N4–Cu1–N8^{ii} 78.69(13), N6–Cu1–N9 93.63(13), N6–Cu1–N6^{i} 90.43(12), N6–Cu1–N8^{ii} 83.86(12), N8^{ii}–Cu1–N9 99.63(12), N9–Cu1–N9^{iii} 78.07(13), N6^{i}–Cu1–N8^{ii} 164.93(11). Symmetry codes: (i) −x, −0.5+y, 0.5−z, (ii) −x, 0.5+y, 0.5−z, (iii) −x, −y, −z.
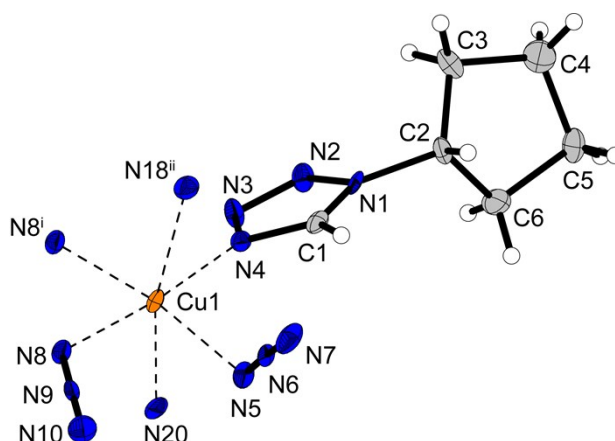
Fig. S7   Coordination environment around the copper(II) centre in **10**. Selected bond lengths (Å): Cu1–N4 1.975(8), Cu1–N5 2.022(8), Cu1–N8 1.994(8), Cu1–N20 2.579(7); select bond angles (°): N4–Cu1–N5 91.1(3), N4–Cu1–N8 174.3(3), N4–Cu1–N20 85.4(3), N5–Cu1–N8 94.2(3), N5–Cu1–N20 85.2(3), N8–Cu1–N20 97.0(3).
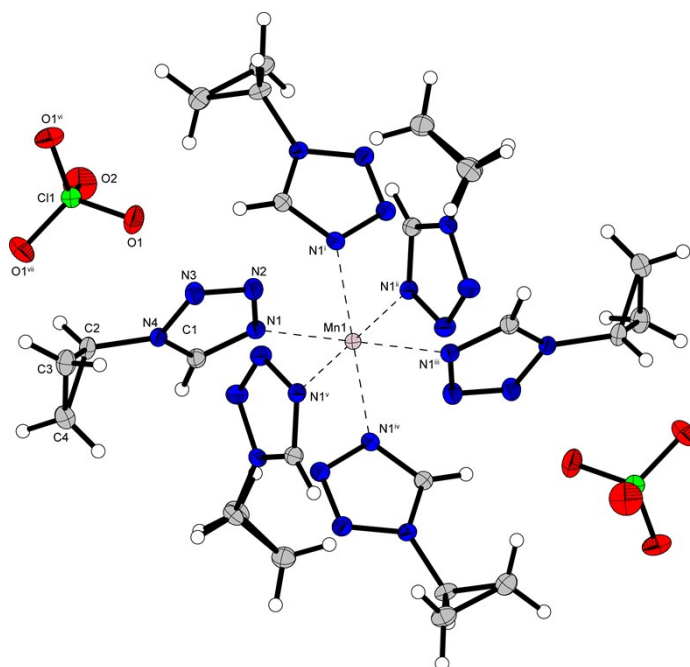
Fig. S8   Molecular unit of **14**. Selected bond length (Å): Mn1–N1 2.2461(15); select bond angles (°): N1–Mn1–N1^i 90.36(5), N1–Mn1–N1^{ii} 90.36(6), N1–Mn1–N1^{iii} 180.00, N1–Mn1–N1^{iv} 89.64(5). Symmetry codes: (i) 0.33333+y, 0.66667−x+y, 0.66667−z, (ii) 1−x+y, 1−x, z, (iii) 1.33333−x, 0.66667−y, 0.66667−z, (iv) 1−y, x−y, z, (v) 0.33333+x−y, −0.33333+x, 0.66667−z.
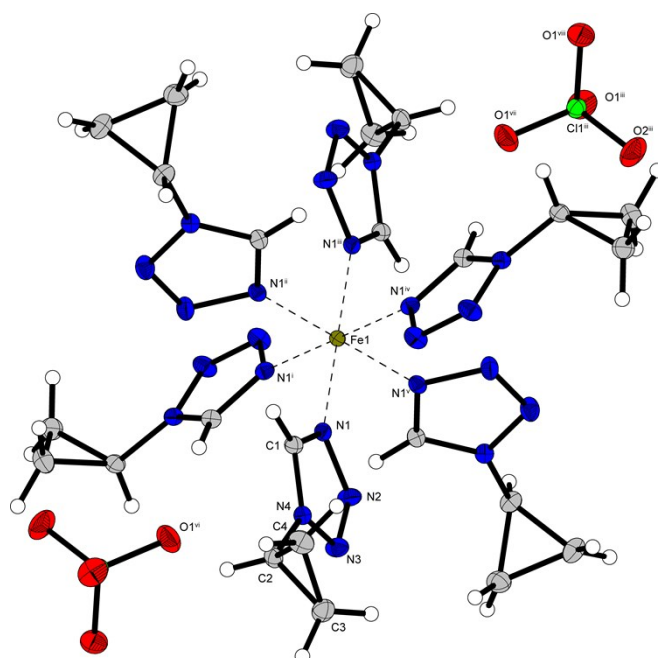

Fig. S9   Molecular unit of **15a** at 107 K. Selected bond length (Å): Fe1–N1 2.0055(15); select bond angles (°): N1–Fe1–N1^i 90.11(7), N1–Fe1–N1^{ii} 90.11(6), N1–Fe1–N1^{iii} 180.00, N1–Fe1–N1^{iv} 89.89(7). Symmetry codes: (i) y, 1−x+y, 1−z, (ii) 1+x−y, x, 1−z, (iii) 2−x, 2−y, 1−z, (iv) 2−y, 1+x−y, z, (v) 1−x+y, 2−x, z.
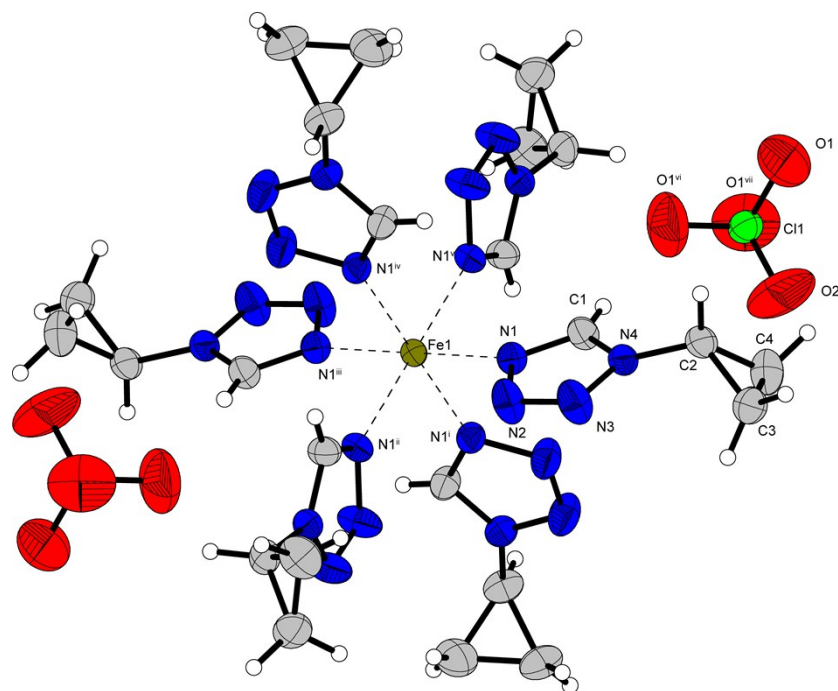
Fig. S10   Molecular unit of **15b** at 297 K. Selected bond length (Å): Fe1–N1 2.190(2); select bond angles (°): N1–Fe1–N1^i 89.82(9), N1–Fe1–N1^{ii} 89.82(8), N1–Fe1–N1^{iii} 180.00, N1–Fe1–N1^{iv} 90.18(9). Symmetry codes: (i) 1−x+y, 2−x, z, (ii) 2−y, 1+x−y, z, (iii) 2−x, 2−y, 1−z, (iv) 1+x−y, x, 1−z, (v) y, 1−x+y, 1−z.
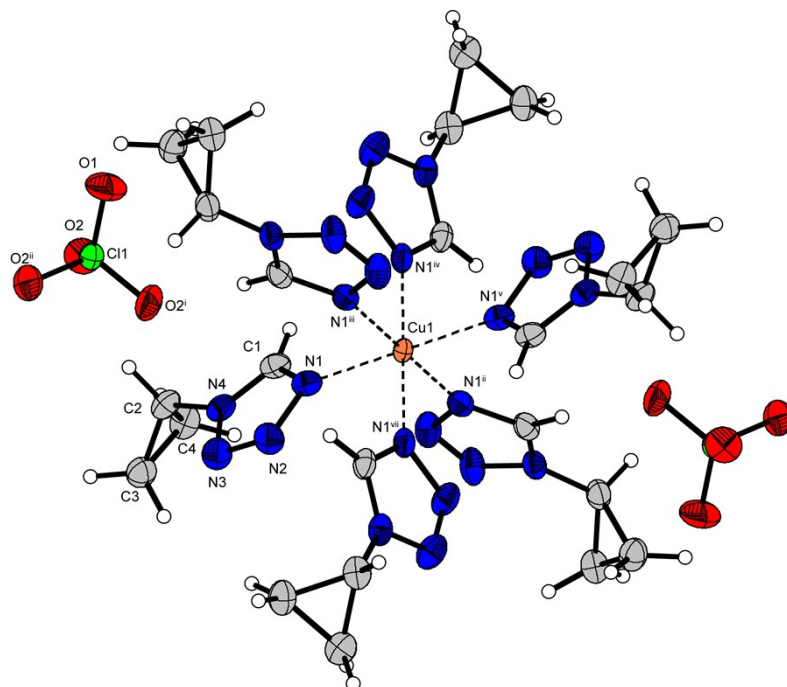
Fig. S11   Molecular unit of **16**. Selected bond length (Å): Cu1–N1 2.128(2); select bond angles (°): N1–Cu1–N1^{ii} 90.05(9), N1–Cu1–N1^{iii} 90.05(9), N1–Cu1–N1^{iv} 180.00, N1–Cu1–N1^v 89.95(9). Symmetry codes: (i) 1−y, x−y, z, (ii) −y, x−y, z, (iii) y, −x+y, 1−z, (iv) x−y, x, 1−z, (v) −x, −y, 1−z, (vi) −x+y, −x, z.
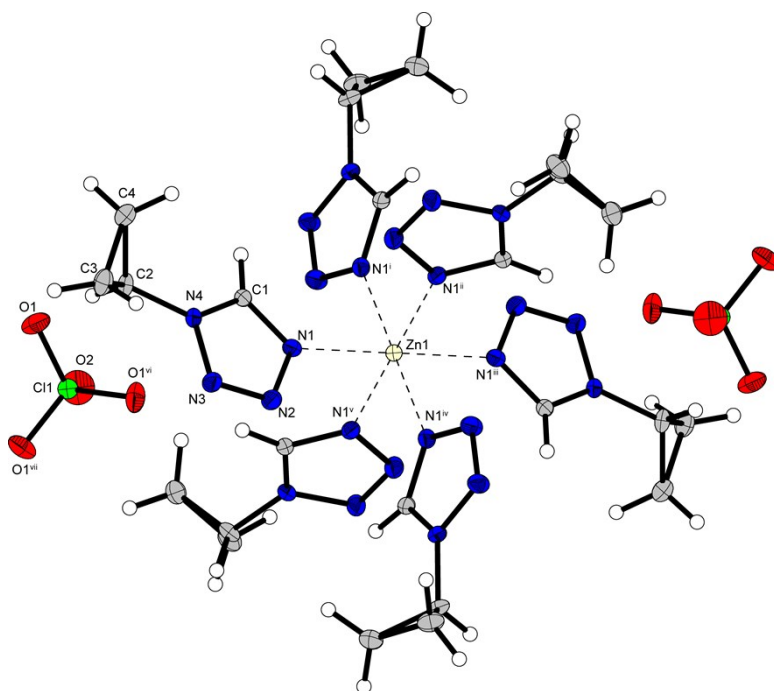
Fig. S12   Molecular unit of **17**. Selected bond length (Å): Zn1–N1 2.159(2); select bond angles (°): N1–Zn1–N1^{i} 90.17(9), N1–Zn1–N1^{ii} 90.17(8), N1–Zn1–N1^{iii} 180.00, N1–Zn1–N1^{iv} 89.83(9). Symmetry codes: (i) y, 1−x+y, 1−z, (ii) 1−x+y, 2−x, z, (iii) 2−x, 2−y, 1−z, (iv) 2−y, 1+x−y, z, (v) 1+x−y, x, 1−z.
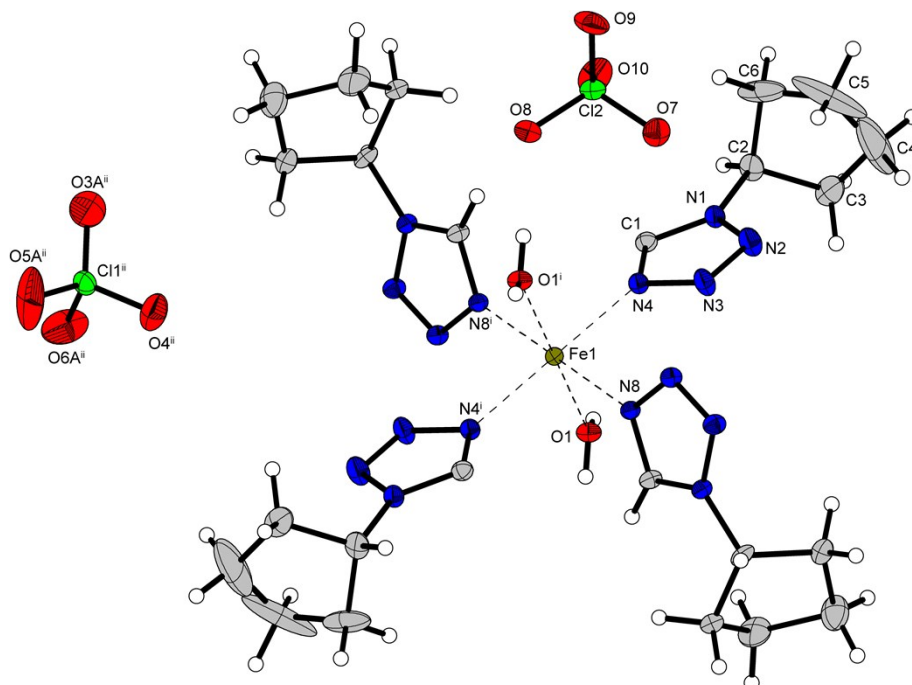

Fig. S13   Molecular unit of **21**. Selected bond lengths (Å): Fe1–O1 2.084(2), Fe1–N4 2.179(2), Fe1–N8 2.229(2); select bond angles (°): O1–Fe1–N4 87.35(9), O1–Fe1–N8 87.44(9), O1–Fe1–O1^{i} 180.00, O1–Fe1–N4^{i} 92.65(9), N4–Fe1–N8 93.30(9). Symmetry codes: (i) 1−x, 1−y, 1−z, (ii) 1−x, 2−y, 1−z.

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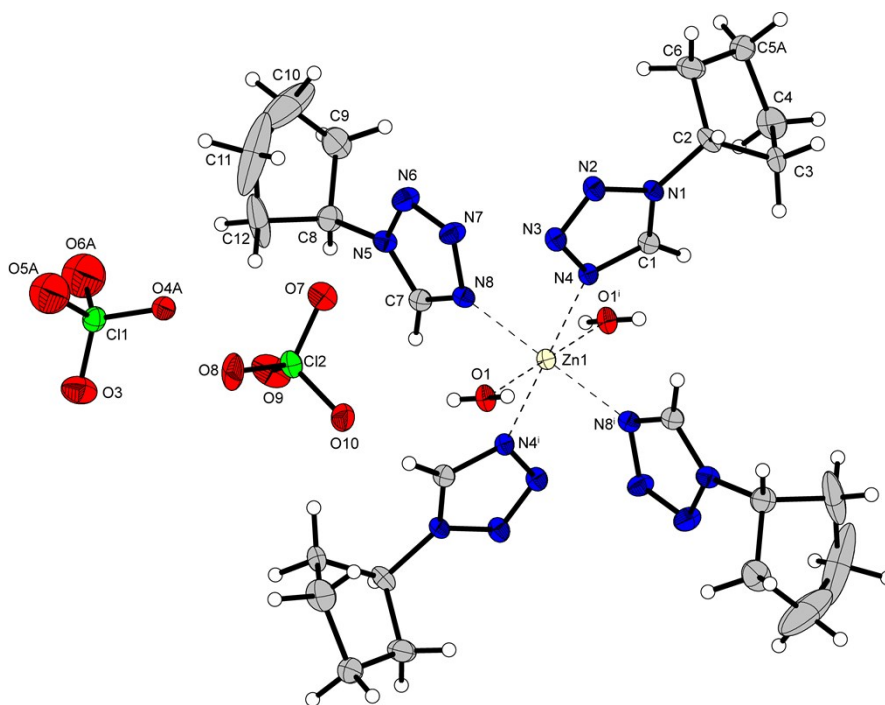
Fig. S14 Molecular unit of **22**. Selected bond lengths (Å): Zn1–O1 2.103(4), Zn1–N4 2.203(4), Zn1–N8 2.129(4); select bond angles (°): O1–Zn1–N4 92.85(14), O1–Zn1–N8 92.51(15), O1–Zn1–O1^i 180.00, O1–Zn1–N4^i 87.15(14). Symmetry codes: (i) 1−x, 2−y, 1−z, (ii) 1−x, 1−y, 1−z.
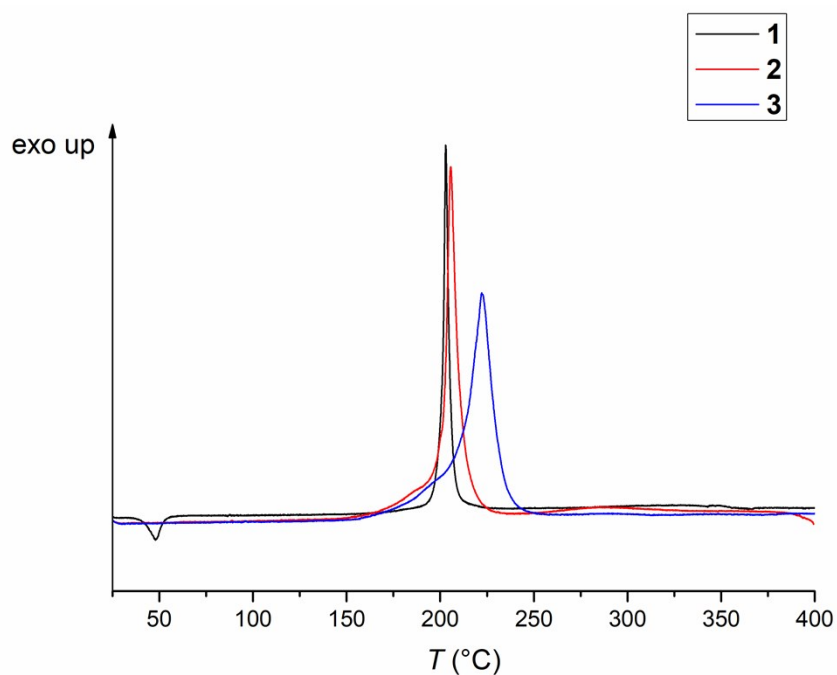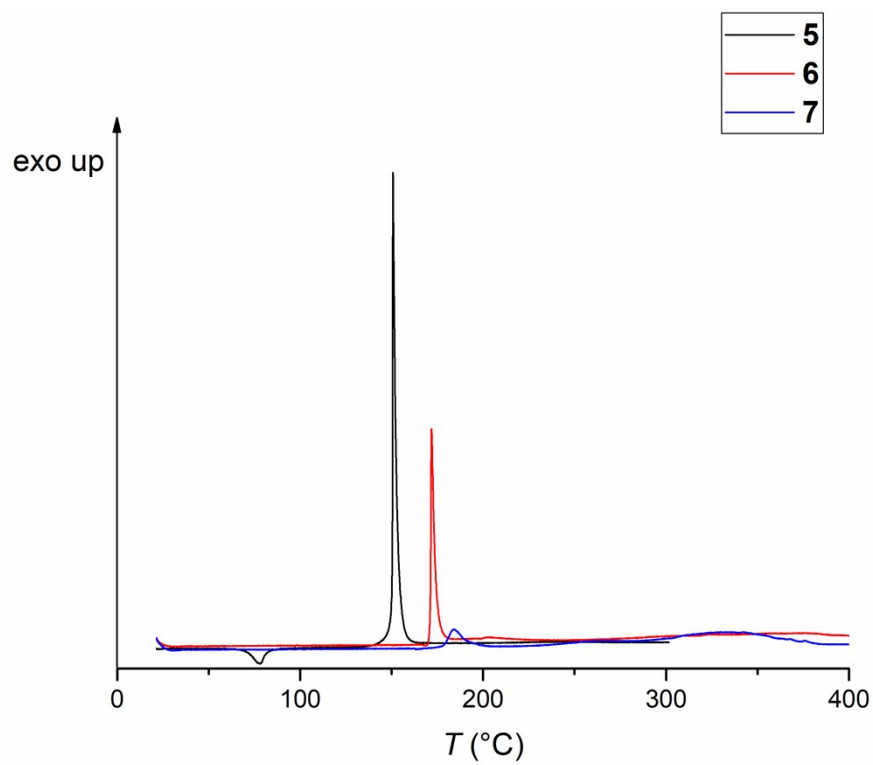
4. DTA plots

Fig. S15 DTA plots of ligands **1**–**3**.

Fig. S16 DTA plots of nitrate complexes **5–7**.
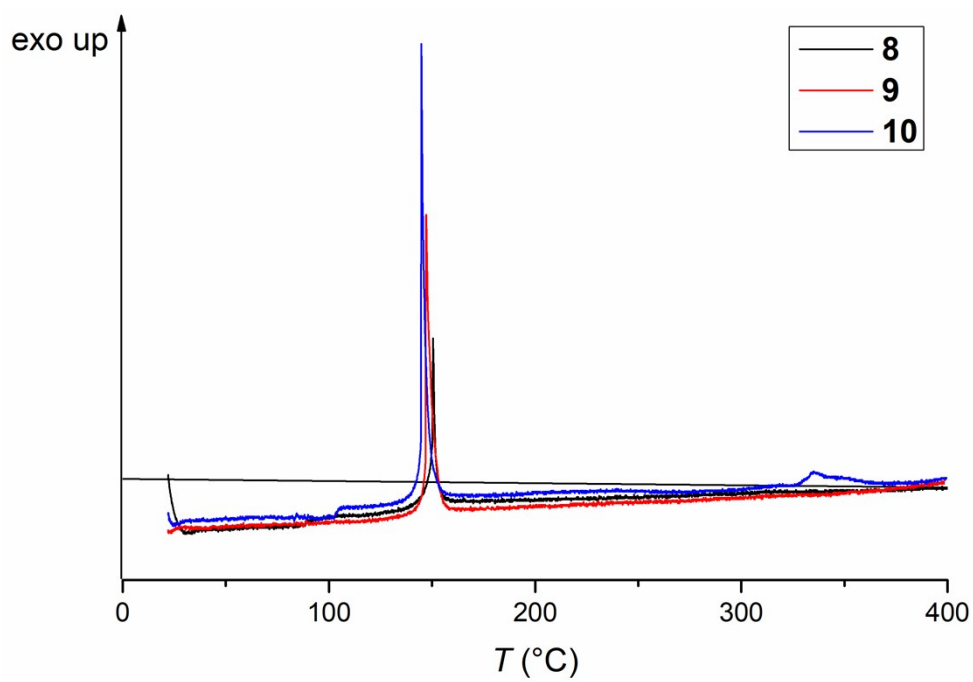

Fig. S17 DTA plots of azide complexes **8–10**.
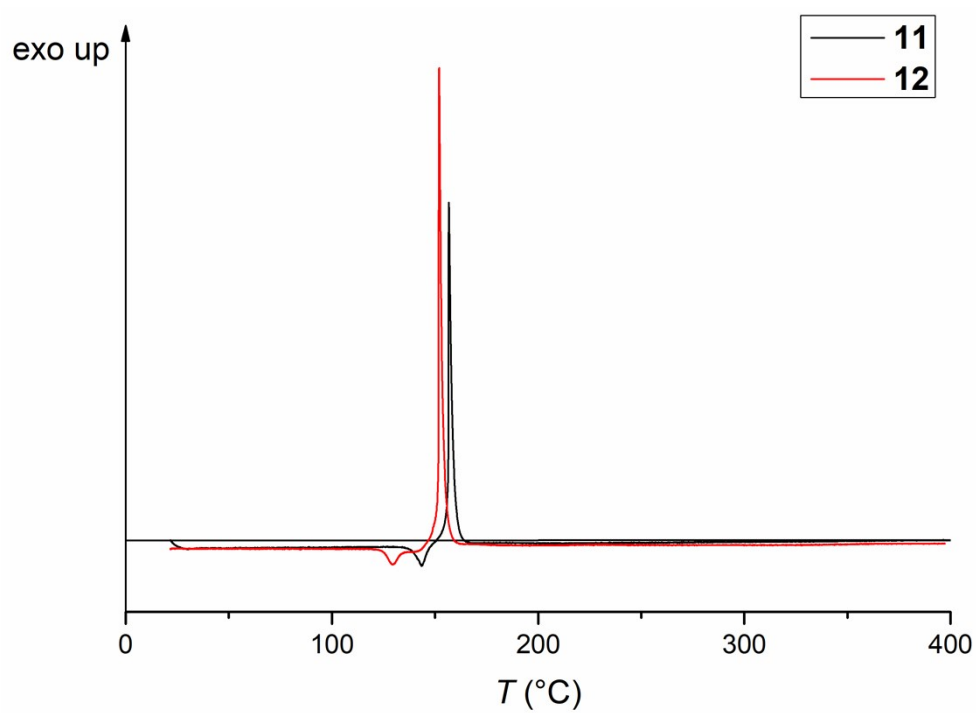
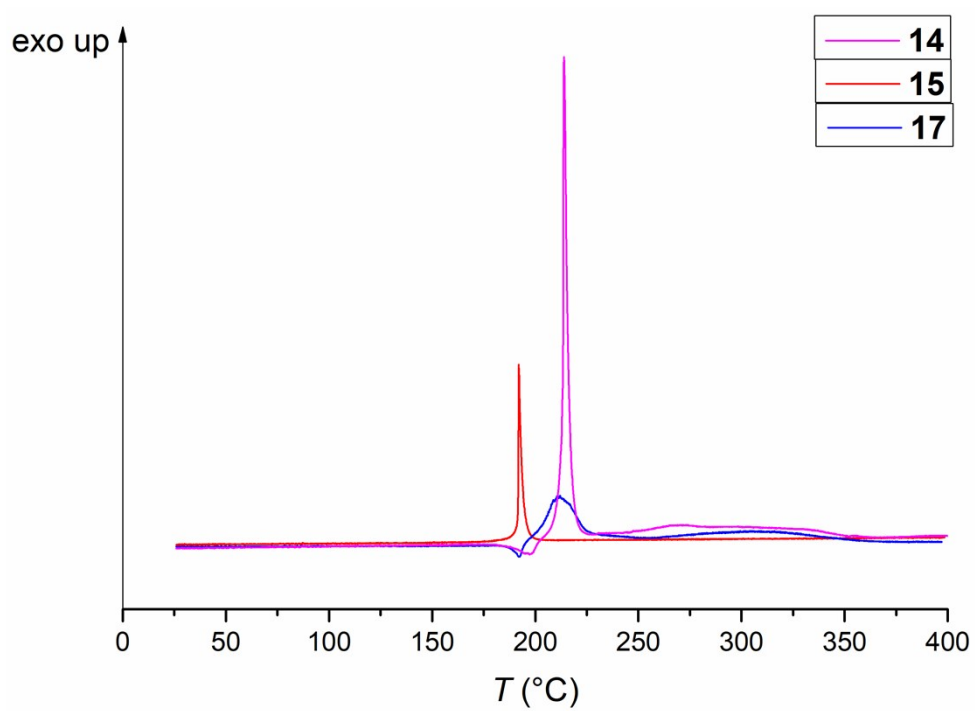**Fig. S18**   DTA plots of chlorate complexes **11** and **12**.

Fig. S19   DTA plots of perchlorate complexes **14**, **15**, and **17**.
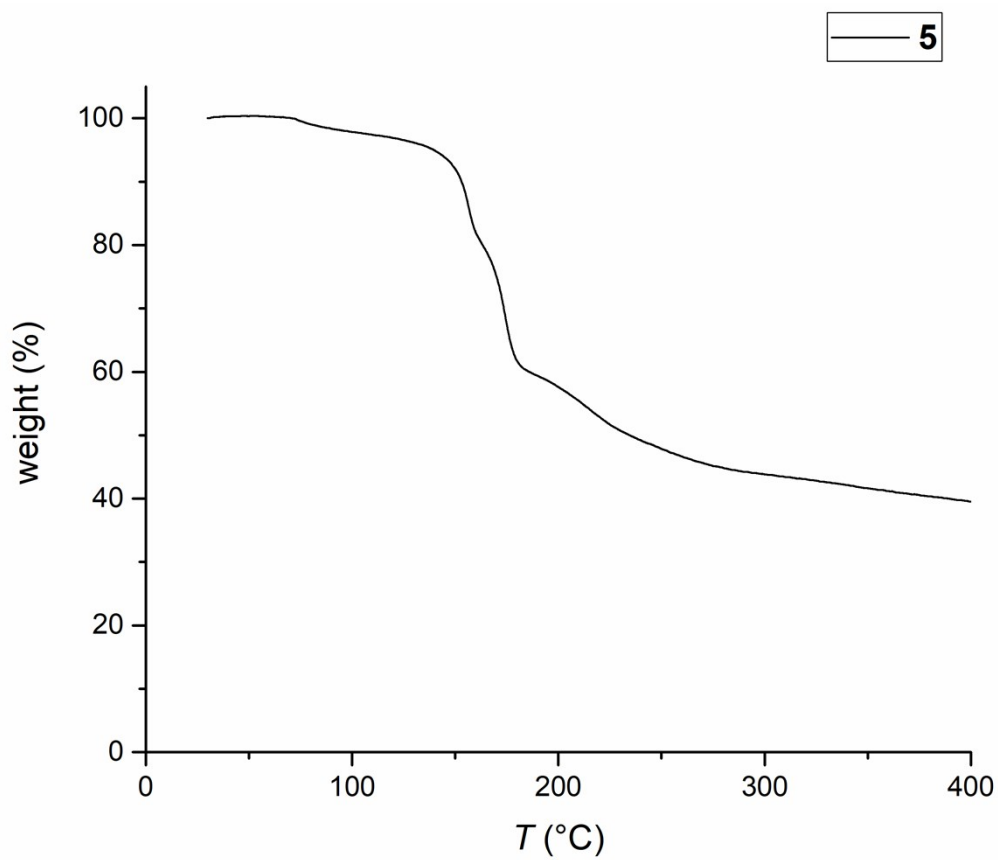
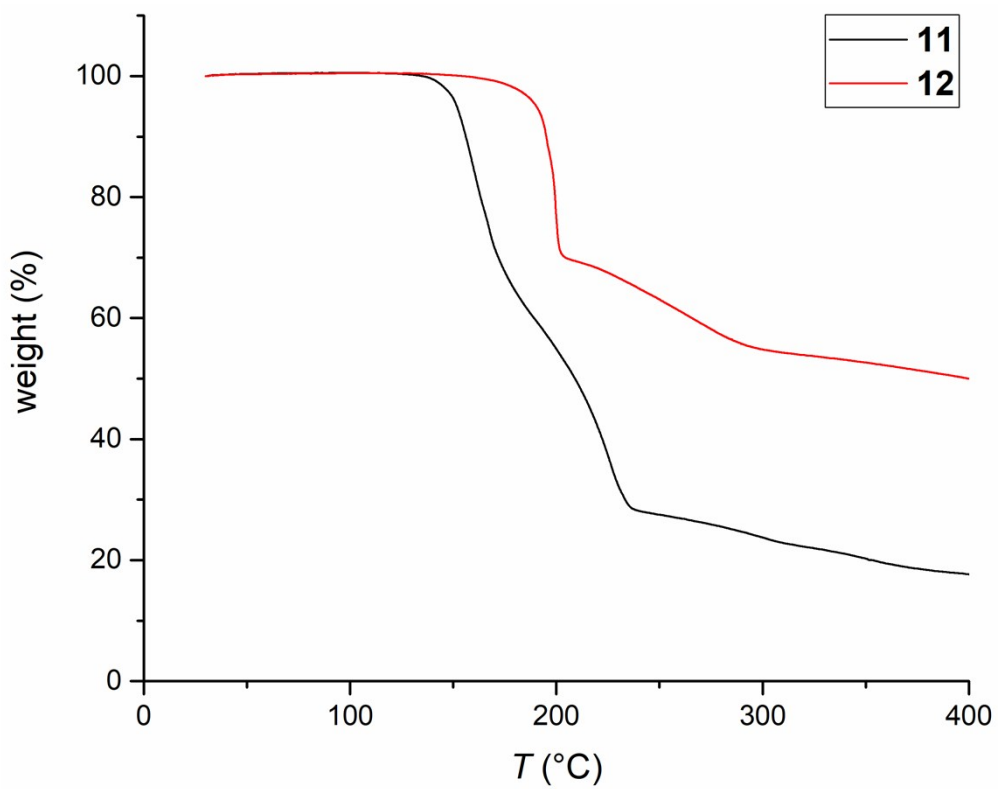## 5. TGA plots

Fig. S20 TGA plot of **5**.

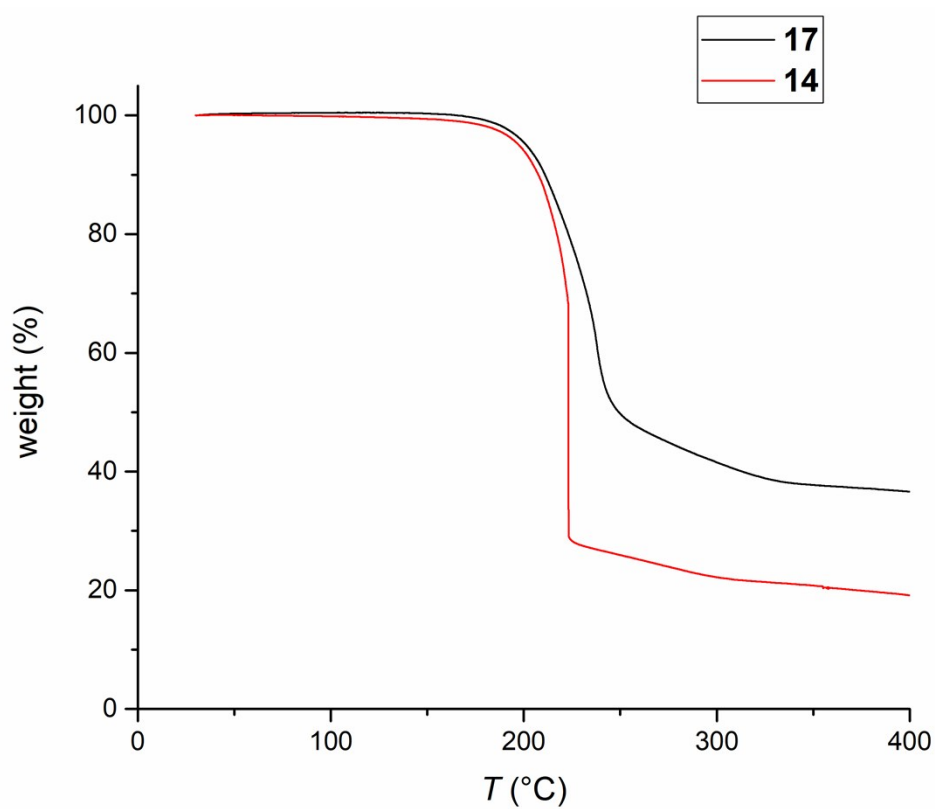**Fig. S21** TGA plots of **11** and **12**.

Fig. S22   DTA plots of **14** and **17**.

6.   Hot Plate and Hot Needle Tests

Fig. S23   Hot plate (left) and hot needle (right) tests of nitrate complex **5**.

Fig. S24   Hot plate (left) and hot needle (right) tests of azide complex **9**.

Fig. S25   Hot plate (left) and hot needle (right) tests of azide complex **10**.

Fig. S26   Deflagrations of ECC **11** and **12** during HP tests.
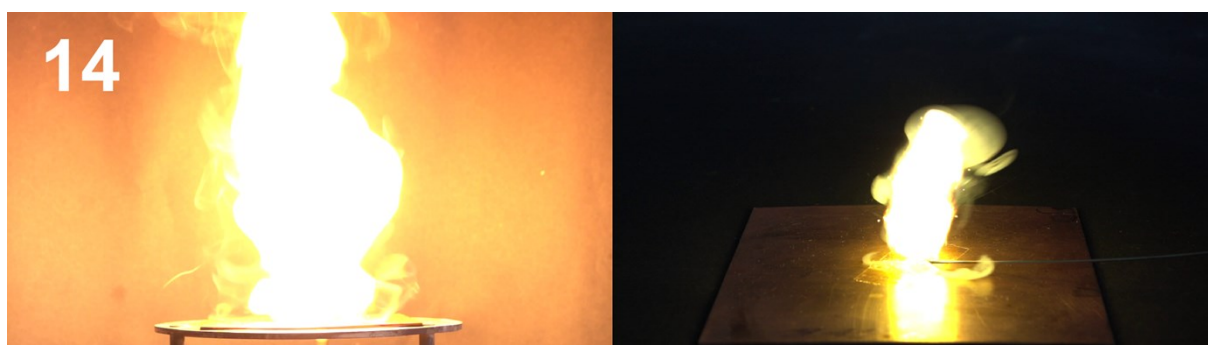
Fig. S27   Hot plate (left) and hot needle (right) tests of manganese complex **14**.
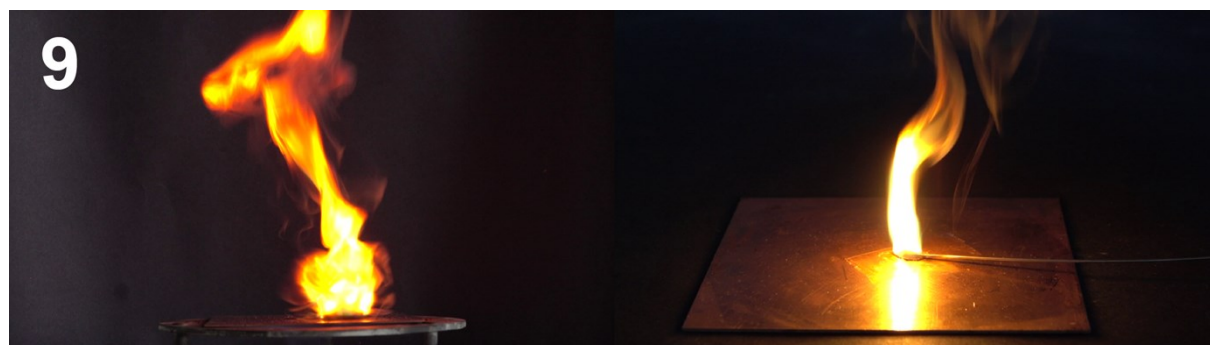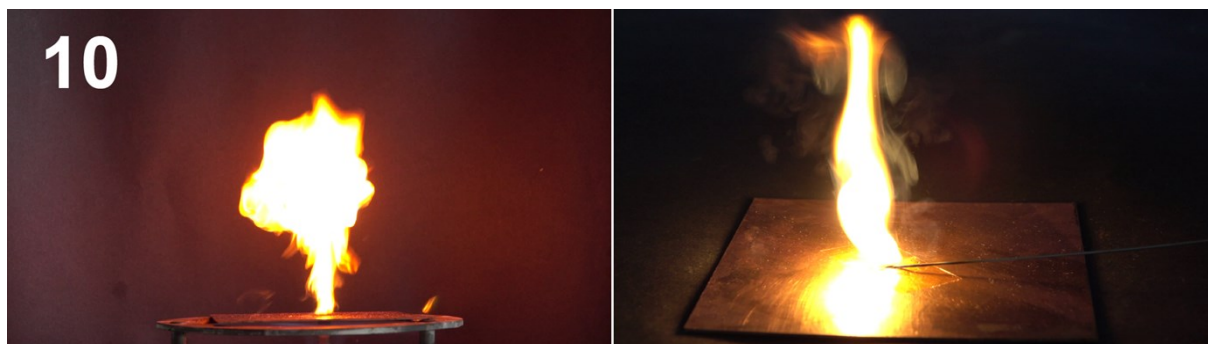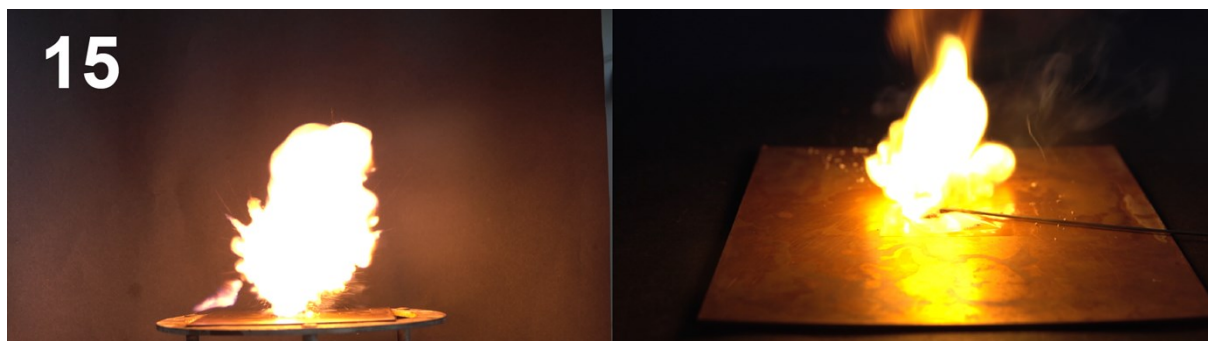

Fig. S28   Hot plate (left) and hot needle (right) tests of iron complex **15**.
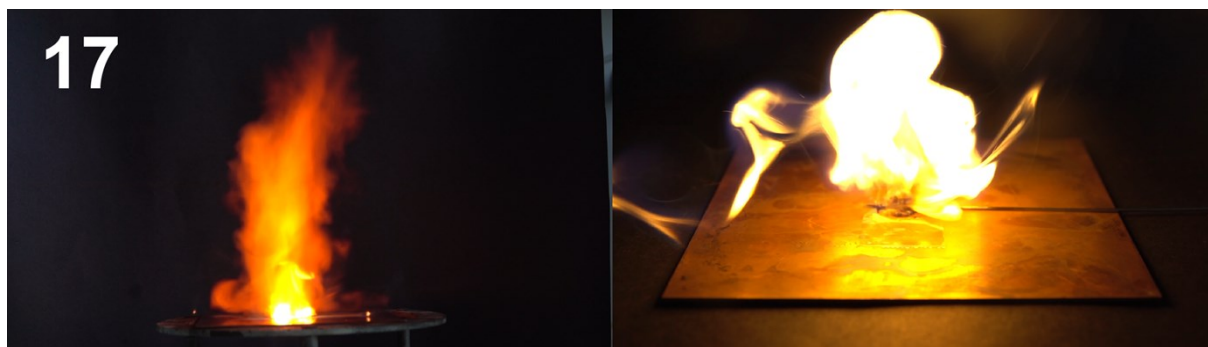
Fig. S29   Hot plate (left) and hot needle (right) tests of zinc complex **17**.

Fig. S30   Results of the hot plate tests of copper perchlorate compounds **16**, **18**, and **19**.

7.   Magnetic Properties

Fig. S31 $[Fe(C_3tz)_6](ClO_4)_2$ (**15**) at room temperature (A) and cooled with liquid nitrogen (B, C) revealing a thermochromic effect.
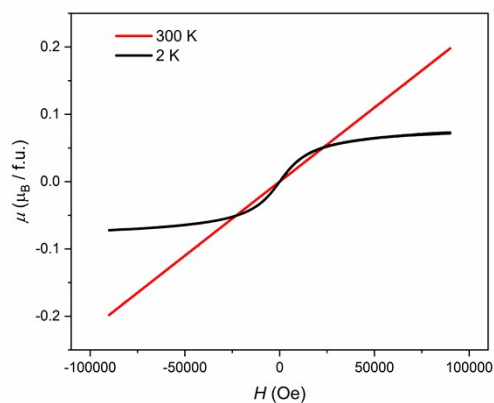
Fig. S32   Magnetization isotherms of $[Fe(C_3tz)_6](ClO_4)_2$ at 300 K (red) and 2 K (black) per formula unit.

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8. 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 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, d-CHCl$_3$ or d_3-MeCN as the solvents. The ^{1}H-^{15}N-HMBC NMR spectra were measured with a data matrix of 1024 × 256, an applied zero filling of 2048 × 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 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). Impact sensitivity tests were carried out according to STANAG 4489[S9] with a modified instruction[S10] using a BAM (Bundesanstalt für Materialforschung) drop hammer.[S11,12] Friction sensitivity tests were carried out according to STANAG 4487[S13] with a modified instruction[S14] using the BAM friction tester. The classification of the tested compounds results from the "UN Recommendations on the Transport of Dangerous Goods".[S15] 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.[S10] 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. Magnetization measurements were performed with a Quantum Design Inc. physical property measurement system (PPMS) equipped with a vibrating sample magnetometer. Data were collected between temperatures of 2-300 K at field

strengths of ±90 kOe with the PPMS MultiVu software package.[S16] A diamagnetic correction accounting for the organic part of the sample.[S17]

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

Procedures for the preparation of the tetrazole ligands

1-cyclopropyl-5*H*-tetrazole (C$_3$tz, 1)

According to a modified literature procedure,[S18] glacial acetic acid (40.0 mL, 0.70 mol, 7.0 equiv.) was added dropwise to a suspension of cyclopropylamine (6.92 mL, 0.10 mol, 1.0 equiv.), sodium azide (7.20 g, 0.11 mol, 1.1 equiv.) and triethyl orthoformate (44 mL, 0.3 mol, 3.0 equiv.) at 50 °C under continuous stirring. The resulting slightly yellow suspension was stirred at 90 °C for 4.5 h. After the mixture was cooled to room temperature concentrated hydrochloric acid (7.29 mL) and water (50 mL) were added. The product was extracted with EtOAc (3 x 70 mL). The combined organic layers were treated with water (100 mL), NaHCO$_3$ solution (50 mL) and brine (50 mL) and dried over Na$_2$SO$_4$. The solvent was evaporated under reduced pressure and the obtained crude 1-cyclopropyl-5*H*-tetrazole (C$_3$tz, **1**) was recrystallized from methanol (5 mL) at room temperature yielding ligand **1** as colourless needles (5.44 g, 49.4 mmol, 49%).

DTA onset (5 °C min^{-1}): 42 °C (endothermic), 200 °C (exothermic.); **IR** (ATR, cm^{-1}): ṽ = 3126 (s), 3069 (vw), 3032 (vw), 2955 (w), 1784 (w), 1718 (w), 1501 (w), 1484 (s), 1463 (m), 1418 (s), 1394 (w), 1355 (m), 1271 (w), 1242 (w), 1209 (s), 1182 (vs), 1097 (vs), 1077 (s), 1063 (s), 1041 (s), 1018 (m), 961 (vs), 949 (m), 894 (s), 875 (s), 838 (s), 783 (w), 722 (m), 677 (vs), 622 (vs), 466 (w); **^{1}H NMR** (CDCl$_3$, 25 °C, ppm) δ: 8.63 (s, 1H), 3.78 (m, 1H), 1.28 (m, 4H); **^{13}C NMR** (CDCl$_3$, 25 °C, ppm) δ: 143.27, 29.44, 7.10. **^{1}H-^{15}N-HMBC NMR** (MeCN-*d$_3$*, 25 °C, ppm) δ: −7.7 (N3), −56.6 (N2), −71.5 (N4), −157.5 (N1); **EA** (C$_4$H$_6$N$_4$, 110.12) calcd.: C 43.63, H 5.49, N 50.88%, found: C 43.53, H 5.09, N 50.85%; **BAM drop hammer**: >40 J, **friction tester:** >360 N; **ESD:** 750 mJ (at grain size >1000 µm).

1-cyclobutyl-5*H*-tetrazole (C$_4$tz, 2)

According to a modified literature procedure,[S18] glacial acetic acid (143 mL, 2.5 mol, 50.0 equiv.) was added dropwise to a suspension of cyclobutylamine hydrochloride (5.38 mL, 0.05 mol, 1.0 equiv.), sodium azide (4.88 g, 0.075 mol, 1.5 equiv.), and triethyl orthoformate (12.5 mL, 0.075 mol, 1.5 equiv.) at 50 °C under continuous stirring. The resulting slightly yellow suspension was stirred at 90 °C for 48 h. After the mixture was cooled to room temperature hydrochloric acid (250 mL, 2M) was added to the suspension. Purification was carried out analogously to **1**. After solvent evaporation under reduced pressure the pure 1-cyclobutyl-5*H*-tetrazole was obtained as yellow oil (3.56 g, 28.7 mmol, 57%).

DTA onset (5 °C min^{-1}): 202 °C (exothermic); **IR** (ATR, cm^{-1}): $\tilde{\upsilon}$ = 3194(m), 2960(s), 2847(s), 2192(w), 2162(s), 2154(s), 2027(w), 2010(vw), 1872(w), 1698(w), 1664(w), 1657(w), 1609(w), 1539(m), 1471(m), 1428(s), 1418(s), 1350(w), 1333(m), 1283(vs), 1257(s), 1228(vs), 1228(vs), 1189(vs), 1115(s), 1004(w), 988(w), 968(w), 875(vw), 826(m); **^{1}H NMR** (CDCl$_3$, 25 °C, ppm) δ: 8.63 (s, 1H), 5.08 (m, 1H), 2.62 (m, 4H), 2.02 (m, 2H), **^{13}C NMR** (CDCl$_3$, 25 °C, ppm) δ: 141.38, 52.50, 30.54, 15.29; **^{1}H-^{15}N-HMBC NMR** (MeCN-*d$_3$*, 25 °C, ppm) δ: −8.0 (N3), −34.6 (N2), −71.6 (N4), −150.0 (N1); **EA** (C$_5$H$_8$N$_4$, 124.15) calcd.: C 48.37, H 6.50, N 45.13%, found: C 48.12, H 6.27, N 44.65%; **BAM drop hammer**: >40 J, **friction tester:** >360 N.

1-cyclopentyl-5*H*-tetrazole (C$_5$tz, 3)

According to a modified literature procedure,[S18] glacial acetic acid (199 mL, 3.50 mol, 50.0 equiv.) was added dropwise to a suspension of cyclopentylamine (7.17 mL, 0.07 mol, 1.0 equiv.), sodium azide (6.77 g, 0.10 mol, 1.5 equiv.), and triethyl orthoformate (17.3 mL, 0.10 mol, 1.5 equiv.) at 50 °C under continuous stirring. The resulting slightly yellow suspension was stirred at 90 °C for 48 h. After the mixture was cooled to room temperature hydrochloric acid (350 mL, 2M) was added to the suspension. Purification was carried out analogously to **1** and **2**. After solvent evaporation under reduced pressure the pure 1-cyclopentyl-5*H*-tetrazole was obtained as orange oil (7.69 g, 55.7 mmol, 80%).

DTA onset (5 °C min^{-1}): 202 °C (exothermic.); **IR** (ATR, cm^{-1}): $\tilde{\upsilon}$ = 3141(m), 2959(s), 2875(m), 2160(m), 2151(m), 2037(w), 1873(vw), 1709(w), 1664(w), 1610(w), 1541(m), 1472(m), 1426(s), 1412(s), 1332(m), 1296(s), 1283(s), 1255(s), 1227(vs), 1194(vs), 1105(s), 1025(w), 1025(w), 970(w), 949(w), 876(vw), 826(w), 809(m), 736(m), 708(m); **^{1}H NMR** (DMSO-d$_6$, 25 °C, ppm) δ: 9.45 (s, 1H), 5.06 (m, 1H), 1.96 (m, 4H), 1.74 (m, 4H); **^{13}C NMR** (DMSO-d$_6$, 25 °C, ppm) δ: 142.89, 59.65, 32.55, 32.43; **^{1}H-^{15}N-HMBC NMR** (MeCN-*d$_3$*,

25 °C, ppm) δ: −7.9 (N3), −34.0 (N2), −71.5 (N4), −149.8 (N1); **EA** ($C_6H_{10}N_4$, 138.17) calcd.: C 52.16, H 7.30, N 40.55%, found: C 52.09, H 6.72, N 37.95%; **BAM drop hammer**: >40 J, **friction tester:** >360 N.

$[Cu_2(C_3tz)_8(H_2O)_2](NO_3)_4$ (5)

For the preparation of the nitrate coordination compounds, copper(II) nitrate trihydrate (109 mg, 0.45 mmol, 1.0 equiv.) and C_3tz (297 mg, 2.70 mmol, 6.0 equiv.) were dissolved in ethanol (2 mL) separately and combined at room temperature. The mixture was stirred for 5 min at 80 °C before it was allowed to crystallize at room temperature. A mixture of $[Cu_2(C_3tz)_4(NO_3)_4]$ and $[Cu_2(C_3tz)_8(H_2O)_2](NO_3)_4$ was obtained. After recrystallization in water (3 mL), pure compound $[Cu_2(C_3tz)_8(H_2O)_2](NO_3)_4$ was obtained.

Compound **5** was received as medium blue crystals. Yield: 258 mg (0.40 mmol, 89%).

DTA onset (5 °C min^{-1}): 71 °C (endothermic), 150 °C (exothermic.); **IR** (ATR, cm^{-1}): ṽ = 3411(w), 3085(m), 2989(w), 1748(vw), 1628(w), 1574(vw), 1513(m), 1459(w), 1421(m), 1381(s), 1337(vs), 1329(vs), 1221(s), 1207(m), 1194(m), 1178(w), 1154(w), 1100(s), 1086(s), 1036(m), 1011(m), 951(w), 920(w), 920(w), 880(w), 829(m), 797(vw), 715(vw), 672(m), 631(m), 526(w), 476 (w), 404 (w); **EA** ($C_{16}H_{26}CuN_{18}O_7$, 646.05): calcd.: C 29.75, H 4.06, N 39.03%, found: C 29.65, H 4.06, N 39.12%; **BAM drop hammer**: >40 J, **friction tester:** >360 N; **ESD:** 1 J (at grain size >1000 μm).

$[Cu(C_4tz)_3(NO_3)_2]$ (6)

Copper(II) nitrate trihydrate (109 mg, 0.45 mmol, 1.0 equiv.) and C_4tz (335 mg, 2.70 mmol, 6.0 equiv.) were dissolved in ethanol separately and combined at room temperature. The mixture was stirred for 5 min at 80 °C before it could crystallize at room temperature to obtain the crude product. Recrystallization in ethanol (3 mL) yielded pure complex **6** compound as steel blue crystals. Yield: 173 mg (0.31 mmol, 69%).

DTA onset (5 °C min^{-1}): 160 °C (exothermic.); **IR** (ATR, cm^{-1}): ṽ = 3134(w), 3126(w), 3000(w), 2957(w), 1572(vw), 1481(m), 1459(s), 1431(s), 1361(w), 1342(w), 1297(s), 1287(vs), 1252(m), 1233(w), 1186(m), 1165(m), 1113(s), 1091(m), 1048(w), 1021(s), 1012(s), 994(m), 950(w), 950(w), 893(m), 837(w), 812(m), 743(w), 728(w), 720(m), 672(s), 599(vw); **EA** ($C_{15}H_{24}CuN_{14}O_6$, 560.00) calcd.: C 32.17, H 4.32, N 35.02%, found: C 32.21, H 4.16, N 35.10%; **BAM drop hammer**: 9 J, **friction tester:** >360 N; **ESD:** 90 mJ (at grain size 500–1000 μm).

[Cu(C₅tz)₂(NO₃)₂] (7)

Copper(II) nitrate trihydrate (109 mg, 0.45 mmol, 1.0 equiv.) and C_5tz (373 mg, 2.70 mmol, 6.0 equiv.) were dissolved in acetonitrile separately and combined at room temperature. The mixture was stirred for 5 min at 80 °C before it was allowed to crystallize at room temperature to obtain the crude product. Recrystallization in ethanol (3 mL) yielded pure complex compound. ECC **7** was crystallized as steel blue crystals. Yield: 49 mg (0.11 mmol, 23%).

DTA onset (5 °C min⁻¹): 165 °C (exothermic.); **IR** (ATR, cm⁻¹): $\tilde{v}$ = 3143(m), 2957(m), 2876(w), 1765(vw), 1722(vw), 1572(vw), 1500(s), 1477(vs), 1454(s), 1372(m), 1260(vs), 1186(s), 1155(s), 1097(s), 1038(m), 1012(vs), 960(m), 947(m), 887(m), 810(s), 749(m), 708(w), 668(m), 668(m), 519(vw); **EA** ($C_{12}H_{20}CuN_{10}O_6$, 463.90) calcd.: C 31.07, H 4.35, N 30.19%, found: C 30.99, H 4.35, N 30.18%; **BAM drop hammer**: <40 J, **friction tester:** >360 N; **ESD:** 750 mJ (at grain size >1000 μm).

General procedure for the preparation of copper(II) azide complexes 8–10

Copper(II) nitrate trihydrate (60.4 mg, 0.25 mmol, 1.0 equiv.), and the respective amounts of ligand (**1**: 55.0 mg, 0.50 mmol, 2.0 equiv.; **2**: 31.0 mg, 0.25 mmol, 1.0 equiv.; **3**: 69.0 mg, 0.50 mmol, 2.0 equiv.) were dissolved in water (4 mL), except ligand **3** which was dissolved in 4 mL water/ethanol 1/1. Sodium azide (32.5 mg, 0.50 mmol, 2.0 equiv.) dissolved in 2 mL water was added dropwise at room temperature while stirring and the complexes started precipitating as brown precipitates. The compounds were filtered off and washed with water.

[Cu(C₃tz)(N₃)₂] (8)

Complex **8** was obtained in the form of a brown solid. Yield: 45.2 mg (0.18 mmol, 70%).

DTA onset (5 °C min⁻¹): 149 °C (exo.); **IR** (ATR, cm⁻¹): $\tilde{v}$ = 3114 (w), 2095 (vs), 2053 (vs), 1814 (vw), 1505 (w), 1454 (w), 1429 (vw), 1417 (w), 1369 (w), 1349 (w), 1297 (m), 1215 (w), 1185 (m), 1165 (vw), 1095 (m), 1079 (w), 1060 (w), 1038 (m), 1010 (m), 951 (vw), 911 (w), 879 (w), 834 (m), 692 (w), 669 (m), 655 (w), 622 (w), 594 (w), 586 (w), 472 (vw), 412 (w); **EA** ($C_4H_6CuN_{10}$, 257.71) calcd.: C 18.64, H 2.35, N 54.35%, found: C 18.65, H 2.45, N 54.29%; **BAM drop hammer**: <1 J, **friction tester:** 5 N; **ESD:** 37 mJ (at grain size <100 μm).

[Cu(C₄tz)(N₃)₂] (9)

ECC **9** was received as brown solid. Yield: 51.5 mg (0.19 mmol, 76%).

DTA onset (5 °C min^{-1}): 148 °C (exothermic); **IR** (ATR, cm^{-1}): $\tilde{\upsilon}$ = 3365 (vw), 3323 (vw), 3128 (w), 2998 (vw), 2961 (vw), 2095 (s), 2048 (vs), 1572 (vw), 1501 (m), 1478 (w), 1458 (vw), 1436 (vw), 1368 (w), 1342 (w), 1288 (m), 1247 (w), 1230 (w), 1199 (w), 1177 (m), 1120 (m), 1088 (m), 1036 (w), 1022 (m), 947 (vw), 724 (w), 693 (w), 670 (m), 659 (w), 603 (w), 586 (w), 556 (vw), 430 (w), 414 (w); **EA** ($C_5H_8CuN_{10}$, 271.74) calcd.: C 22.10, H 2.97, N 51.55%, found: C 21.86, H 2.79, N 51.35%; **BAM drop hammer**: 8 J, **friction tester:** 60 N; **ESD:** 50 mJ (at grain size <100 μm).

[Cu(C$_5$tz)(N$_3$)$_2$] (10)

Azide complex **10** precipitated as brown solid. Yield: 49.5 mg (0.17 mmol, 68%).

DTA onset (5 °C min^{-1}): 145 °C (exothermic); **IR** (ATR, cm^{-1}): $\tilde{\upsilon}$ = 3363(vw), 3315(vw), 3131(w), 2964(w), 2876(w), 2085(s), 2073(s), 2039(vs), 1503(m), 1476(w), 1449(w), 1375(w), 1343(w), 1315(w), 1293(m), 1277(m), 1180(m), 1153(w), 1094(m), 1037(w), 1018(m), 951(w), 951(w), 906(w), 886(w), 821(vw), 771(w), 689(w), 673(m), 660(w);**EA** ($C_6H_{10}CuN_{10}$, 257.71) calcd.: C 25.22, H 3.53, N 49.02%, found: C 25.34, H 3.67, N 48.49%; **BAM drop hammer**: 5 J, **friction tester:** 216 N; **ESD:** 76 mJ (at grain size <100 μm).

General procedure for preparation of copper(II) chlorate complexes

Barium chlorate monohydrate (145 mg, 0.45 mmol, 1.0 equiv.) and copper(II) sulphate pentahydrate (112 mg, 0.45 mmol, 1.0 equiv.) were dissolved in water (5 mL), combined and stirred for 5 min. The mixture was cooled to 0 °C and the precipitated barium sulphate, filtered off. The solvent was evaporated under reduced pressure and pure copper(II) chlorate was dissolved in ethanol (2 mL). The respective amounts of ligand (**1**: 297 mg, 2.70 mmol, 6.0 equiv.; **2**: 335 mg, 2.70 mmol, 6.0 equiv.; **3**: 373 mg, 2.70 mmol, 6.0 equiv.) were each dissolved in ethanol (2 mL), and added dropwise to the dissolved copper salt while stirring at room temperature. The reaction mixture was stirred for 5 min at 80 °C before it was allowed to crystallize at room temperature. Crystallization process took up 1–2 days. The compounds were filtered off before complete evaporation of the solvent and were washed with cold ethanol.

[Cu(C$_3$tz)$_6$](ClO$_3$)$_2$ (11)

Complex **11** crystallized as sky blue hexagonal plates overnight. Yield: 215 mg (0.24 mmol, 53%).

DTA onset (5 °C min^{-1}): 138 °C (endothermic), 156 °C (exothermic); **IR** (ATR, cm^{-1}): $\tilde{\upsilon}$ = 3102 (m), 3063 (w), 3017 (vw), 2986 (w), 1572 (vw), 1505 (m), 1460 (vw), 1429 (w), 1420 (m), 1363 (w), 1304 (vw), 1224 (m), 1199 (m), 1187 (m), 1171 (vw), 1115 (w), 1102 (s), 1079 (w), 1060 (w), 1038 (m), 1029 (w), 1007 (m), 968 (vs), 936 (s), 876 (m), 840 (m), 777 (w), 720 (w), 672 (s), 621 (s), 608 (m), 473 (m); **EA** ($C_{24}H_{36}Cl_2CuN_{24}O_6$, 907.20) calcd.: C 32.35, H 4.07, N 37.72%, found: C 32.34, H 3.77, N 37.84%; **BAM** drop hammer: 2 J, **friction tester:** 32 N; **ESD:** 100 mJ (at grain size 500–1000 μm).

Alternatively, it was also possible to precipitate $[Cu(C_3tz)_6](ClO_3)_2$ directly from the solution. After combination of the dissolved copper salt and ligand **1** at room temperature, the complex compound directly precipitated, filtered off and washed with cold ethanol. ECC **11** was obtained in form of a light blue powder. Yield: 274 mg (0.30 mmol, 67%),

$[Cu(C_4tz)_4(ClO_3)_2]$ (12)

Compound **12** was received over night in the form of steel blue crystals. Yield: 204 mg (0.28 mmol, 62%).

DTA onset (5 °C min^{-1}): 126 °C (endothermic), 153 °C (exothermic); **IR** (ATR, cm^{-1}): $\tilde{\upsilon}$ = 3137 (w), 3123 (w), 2991 (w), 2953 (w), 1572 (vw), 1500 (m), 1482 (w), 1459 (w), 1446 (w), 1437 (w), 1360 (w), 1306 (w), 1247 (w), 1234 (w), 1199 (m), 1188 (m), 1168 (w), 1124 (m), 1101 (m), 1086 (m), 1022 (m), 987 (s), 952 (s), 902 (vs), 842 (m), 793 (w), 731 (m), 716 (m), 664 (m), 603 (m), 560 (w), 478 (s), 430 (m); **EA** ($C_{20}H_{32}Cl_2CuN_{16}O_6$, 727.03): calc.: C 33.04, H 4.44, N 30.83%, found: C 32.85, H 4.49, N 30.66%; **BAM drop hammer**: 5 J, **friction tester:** 36 N; **ESD:** 200 mJ (at grain size 100–500μm).

Perchlorate complexes

The respective amount of the transition metal salt (0.45 mmol, Mn(ClO$_4$)$_2$·6 H$_2$O: 163 mg; Fe(ClO$_4$)$_2$·6 H$_2$O: 163 mg, 1.0 equiv.; Cu(ClO$_4$)$_2$·6 H$_2$O: 167 mg, 1.0 equiv.; Zn(ClO$_4$)$_2$·6 H$_2$O: 168 mg;) and C$_3$tz (297 mg, 2,70 mmol, 6.0 equiv.) were each dissolved in ethanol. The ligand solution was added dropwise to the dissolved metal salt while stirring at room temperature. The reaction mixtures were stirred at 80 °C and in case of iron, copper, and zinc, more ethanol was added to completely dissolve the formed precipitate. After 5 min the reaction mixtures were allowed to crystallize at room temperature. Crystallization process took 1 h up to 2 days. The compounds were filtered off before complete evaporation of the solvent and washed with cold ethanol.

[Mn(C₃tz)₆](ClO₄)₂ (14)

ECC **14** was received as colourless crystals. Yield: 338 mg (0.37 mmol, 82%).

DTA onset (5 °C min⁻¹): 188 °C (endothermic), 206 °C (exothermic); **IR** (ATR, cm⁻¹): $\tilde{\upsilon}$ = 3121 (m), 3079 (w), 2980 (vw), 1571 (vw), 1498 (m), 1459 (vw), 1420 (w), 1361 (w), 1341 (vw), 1301 (w), 1225 (m), 1184 (m), 1101 (vs), 1089 (vs), 1070 (vs), 1043 (s), 990 (s), 951 (w), 906 (w), 878 (m), 836 (w), 720 (w), 671 (m), 622 (vs); **EA** ($C_{24}H_{36}Cl_2MnN_{24}O_8$, 914.55) calcd.: C 31.52, H 3.97, N 36.76%, found: C 31.45, H 3.72, N 36.73%; **BAM drop hammer**: 5 J, **friction tester:** 216 N; **ESD:** 90 mJ (at grain size >1000 μm).

[Fe(C₃tz)₆](ClO₄)₂ (15)

Compound **15** was obtained as colourless crystals. Yield: 308 mg (0.33 mmol, 74%).

DTA onset (5 °C min⁻¹): 192 °C (exothermic); **IR** (ATR, cm⁻¹): $\tilde{\upsilon}$ = 3121 (w), 3078 (w), 1571 (vw), 1499 (m), 1458 (w), 1420 (m), 1361 (w), 1300 (w), 1278 (w), 1225 (m), 1184 (m), 1101 (vs), 1089 (vs), 1070 (vs), 1042 (s), 1023 (m), 992 (s), 950 (w), 906 (w), 878 (m), 836 (m), 806 (w), 784 (vw), 720 (w), 671 (s), 622 (vs); **EA** ($C_{24}H_{36}Cl_2FeN_{24}O_8$, 915.46) calcd.: C 31.49, H 3.96, N 36.72%, found: C 31.36, H 3.71, N 36.42%; **BAM drop hammer**: 3 J, **friction tester:** 54 N; **ESD:** 90 mJ (at grain size >1000 μm).

[Cu(C₃tz)₆](ClO₄)₂ (16)

ECC **16** crystallized as deep sky-blue hexagons within 1 h. Yield: 264 mg (0.29 mmol, 64%).

DTA onset (5 °C min⁻¹): 174 °C (endothermic), 183 °C (exothermic); **IR** (ATR, cm⁻¹): $\tilde{\upsilon}$ = 3128 (m), 3079 (w), 1505 (m), 1459 (w), 1420 (m), 1361 (w), 1307 (w), 1227 (m), 1198 (w), 1184 (m), 1100 (vs), 1088 (vs), 1071 (vs), 1041 (s), 1003 (m), 986 (m), 950 (w), 937 (w), 904 (w), 878 (m), 835 (m), 772 (w), 720 (w), 671 (s), 622 (vs), 476 (vw); **EA** ($C_{24}H_{36}Cl_2CuN_{24}O_8$, 923.13) calcd.: C 31.23, H 3.93, N 36.42%, found: C 31.18, H 3.98, N 36.53%; **BAM drop hammer**: 4 J, **friction tester:** 80 N; **ESD:** 480 mJ (at grain size 500–1000 μm).

[Zn(C₃tz)₆](ClO₄)₂ (17)

Complex **17** was obtained as colourless crystals. Yield: 308 mg (0.33 mmol, 74%).

DTA onset (5 °C min⁻¹): 188 °C (endothermic), 201 °C (exothermic); **IR** (ATR, cm⁻¹): $\tilde{\upsilon}$ = 3124 (m), 3079 (w), 1572 (vw), 1501 (m), 1459 (w), 1420 (m), 1361 (w), 1341 (vw), 1302 (w), 1226 (m), 1198 (w), 1184 (m), 1169 (w), 1102 (vs), 1088 (vs), 1071 (vs), 1042 (s), 1025 (m),

995 (s), 950 (w), 937 (w), 907 (w), 878 (m), 836 (m), 772 (vw), 720 (w), 671 (s), 622 (vs), 473 (vw); **EA** ($C_{24}H_{36}Cl_2ZnN_{24}O_8$, 924.99) calcd.: C 31.16, H 3.92, N 36.34 %, found: C 30.89, H 3.71, N 36.08 %; **BAM drop hammer**: 5 J, **friction tester:** 216 N; **ESD:** 90 mJ (at grain size 500–1000 μm).

Copper(II) perchlorate complexes 18 and 19

[Cu(C₄tz)₆(H₂O)](ClO₄)₂ (18)

Copper(II) perchlorate hexahydrate (167 mg, 0.45 mmol, 1.0 equiv.) and C_4tz (335 mg, 2.70 mmol, 6.0 equiv.) were dissolved separately in acetonitrile (1 mL) and combined. The reaction mixture was stirred for 5 min at 80 °C and left to crystallize at room temperature, yielding the complex compound after 2 h. Perchlorate complex **18** was obtained as steel blue crystals: Yield 222 mg (0.29 mmol, 63%).

DTA onset (5 °C min⁻¹): 191 °C (exothermic); **IR** (ATR, cm⁻¹): ṽ = 3492 (w), 3129 (w), 2992 (w), 2958 (w), 2907 (vw), 2869 (vw), 1572 (vw), 1506 (m), 1479 (vw), 1446 (w), 1439 (w), 1352 (w), 1307 (vw), 1254 (vw), 1226 (vw), 1199 (m), 1169 (w), 1090 (vs), 1065 (vs), 1012 (s), 952 (w), 933 (w), 909 (w), 848 (w), 731 (w), 718 (w), 670 (m), 622 (s), 468 (vw), 432 (vw); **EA** ($C_{20}H_{34}Cl_2CuN_{16}O_9$, 777.04) calcd.: C 30.91, H 4.41, N 28.84%, found: C 31.03, H 4.48, N 29.02%; **BAM drop hammer**: 8 J, **friction tester:** 84 N; **ESD:** 250 mJ (at grain size >1000 μm).

[Cu(C₅tz)₄(H₂O)](ClO₄)₂ (19)

Copper(II) perchlorate hexahydrate (167 mg, 0.45 mmol, 1.0 equiv.) and C_5tz (373 mg, 2.70 mmol, 6.0 equiv.) were dissolved separately in ethanol (1 mL). A precipitate was formed after the addition and more ethanol was used (5 mL). The reaction mixture was stirred for 5 min at 80 °C and left to crystallize at room temperature. Compound **19** was obtained as royal blue crystals. Yield: 225 mg (0.27 mmol, 60%). Grain size: >1000 μm.

DTA onset (5 °C min⁻¹): 188 °C (endothermic), 207 °C (exothermic); **IR** (ATR, cm⁻¹): ṽ = 3495 (w), 3131 (w), 2964 (w), 2877 (w), 1639 (vw), 1573 (vw), 1503 (vw), 1452 (w), 1439 (w), 1360 (vw), 1313 (vw), 1208 (w), 1184 (w), 1084 (vs), 1063 (vs), 1016 (m), 931 (w), 898 (m), 679 (w), 622 (s), 419 (vw); **EA** ($C_{24}H_{42}Cl_2CuN_{16}O_9$, 833.15) calcd.: C 34.60, H 5.08, N 26.90%, found: C 34.60, H 4.95, N 26.90%; **BAM drop hammer**: 6 J, **friction tester:** 144 N; **ESD:** 250 mJ (at grain size >1000 μm).

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