Electronic Supplementary Material (ESI) for CrystEngComm.

Cu(II) 3,5-diiodosalicylate complexes: precursor-dependent formation of mono-, di-, tri- and tetranuclear compounds and 1D coordination polymers

Mikhail A. Bondarenko, Pavel A. Abramov, Ilya V. Korolkov, Artem S. Bogomyakov, Maxim N. Sokolov and Sergey A. Adonin

Table S1. Experimental details of XRD

	1	**2**	**3**	**4**	**5**	**6**	**7**
Chemical formula	$C_{26}H_{20}CuI_4N_2O_6$	$C_{26}H_{20}CuI_4N_2O_6$	$C_{24}H_{16}CuI_4N_2O_6$	$C_{37.60}H_{21.20}Cu_2I_8N_{4.80}O_{12}$	$C_{19}H_{17}ClCuI_2N_2O_3$	$C_{21}H_{21}ClCuI_2N_2O_3$	$C_{50}H_{47.80}Cl_4Cu_3I_4N_6O_6$
M_r	1027.58	1027.58	999.53	1874.47	674.14	702.19	1668.76
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$	Tetragonal, $P4/mnc$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Temperature (K)	140	140	140	140	150	142	150
a, *b*, *c* (Å)	9.6199 (7), 9.1882 (5), 17.4611 (11)	24.6536 (8), 13.7854 (5), 8.6860 (3)	7.8509 (3), 8.4157 (5), 10.9695 (6)	11.0664 (6), 11.0664 (6), 23.521 (2)	9.0941 (4), 11.1084 (4), 11.1815 (4)	9.3176 (3), 11.6974 (4), 11.8686 (4)	8.5657 (2), 11.8674 (2), 13.5591 (3)
α, β, γ (°)	90, 104.355 (8), 90	90, 91.111 (3), 90	79.902 (5), 77.108 (4), 87.265 (4)	90, 90, 90	102.305 (3), 103.773 (3), 94.247 (3)	73.151 (3), 71.895 (3), 89.946 (3)	89.250 (1), 85.618 (1), 89.773 (1)
V (Å^3)	1495.19 (17)	2951.47 (18)	695.52 (6)	2880.6 (4)	1062.57 (7)	1171.09 (7)	1374.16 (5)
Z	2	4	1	2	2	2	1
μ (mm^{-1})	4.90	4.97	5.27	5.08	4.08	3.71	3.65
Crystal size (mm)	0.50 × 0.20 × 0.20	0.10 × 0.10 × 0.10	0.20 × 0.10 × 0.10	0.30 × 0.20 × 0.20	0.30 × 0.20 × 0.10	0.40 × 0.20 × 0.20	0.22 × 0.18 × 0.17
Diffractometer	New Xcalibur, AtlasS2	New Xcalibur, AtlasS2	New Xcalibur, AtlasS2	New Xcalibur, AtlasS2	New Xcalibur, AtlasS2	New Xcalibur, AtlasS2	Bruker D8 Venture diffractometer

Absorption correction	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.558, 1.000	0.870, 1.000	0.808, 1.000	0.851, 1.000	0.850, 1.000	0.843, 1.000	0.638, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6888, 3298, 2682	12427, 5588, 5025	5525, 3053, 2623	7099, 1745, 1330	7789, 4028, 3375	10249, 5184, 4267	25560, 8388, 7365
R_{int}	0.032	0.028	0.026	0.026	0.026	0.034	0.026
θ values (°)	θ_{max} = 29.0, θ_{min} = 2.2	θ_{max} = 25.7, θ_{min} = 2.2	θ_{max} = 29.0, θ_{min} = 2.5	θ_{max} = 28.9, θ_{min} = 2.6	θ_{max} = 25.7, θ_{min} = 1.9	θ_{max} = 29.0, θ_{min} = 1.9	θ_{max} = 30.5, θ_{min} = 2.3
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.682	0.610	0.682	0.680	0.610	0.683	0.715
Range of *h*, *k*, *l*	*h* = -9→13, *k* = -12→12, *l* = -23→23	*h* = -26→30, *k* = -16→16, *l* = -10→7	*h* = -9→10, *k* = -9→10, *l* = -10→14	*h* = -14→10, *k* = -7→13, *l* = -28→31	*h* = -11→9, *k* = -13→13, *l* = -13→13	*h* = -11→10, *k* = -11→15, *l* = -14→14	*h* = -12→12, *k* = -16→16, *l* = -19→19
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.089, 1.05	0.069, 0.151, 1.20	0.031, 0.060, 1.03	0.054, 0.157, 1.09	0.040, 0.082, 1.03	0.035, 0.072, 1.01	0.023, 0.054, 1.06
No. of reflections, parameters, restraints	3298, 174, 0	5588, 355, 0	3053, 172, 0	1745, 100, 2	4028, 254, 0	5184, 272, 0	8388, 338, 1
H-atom treatment	H atoms treated by a mixture of	H-atom parameters	H atoms treated by a mixture of	H atoms treated by a mixture of	H-atom parameters	H-atom parameters	H atoms treated by a mixture of

	independent and constrained refinement	constrained	independent and constrained refinement	independent and constrained refinement	constrained	constrained	independent and constrained refinement
	$w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 0.9211P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0061P)^2 + 111.3673P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0189P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0625P)^2 + 21.0843P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0234P)^2 + 3.2727P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0244P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0222P)^2 + 0.3077P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.39, -1.44	3.53, -1.35	0.77, -1.19	1.44, -1.56	1.88, -1.03	1.05, -1.15	0.54, -0.49

	8	**9**	**10**	**11**	**12**	**13**	**14**
Chemical formula	$C_{37.33}H_{40}Cl_{2.67}Cu_2I_{2.67}N_4O_4$	$C_{48}H_{28}Cu_4I_8N_4O_{12}$	$C_{52}H_{36}Cu_4I_8N_4O_{12}$	$C_{52}H_{36}Cu_4I_8N_4O_{12}$	$C_{56}H_{44}Cu_4I_8N_4O_{12}$	$C_{13}H_9CuI_2NO_3$	$C_{15}H_{12}CuI_2N_2O_3$
M_r	1168.74	2122.10	2178.21	2178.21	2234.31	544.55	585.61
Crystal system, space group	Monoclinic, *C*2/*c*	Tetragonal, $I4_1/a$	Tetragonal, $I4_1/a$	Tetragonal, $I4_1/a$	Tetragonal, $I4_1/a$	Monoclinic, $P2_1/c$	Orthorhombic, $P2_12_12_1$
Temperature (K)	150	150	140	150	150	150	150
a, *b*, *c* (Å)	32.1635 (10), 7.9649 (2), 29.8771 (10)	16.9289 (4), 16.9289 (4), 19.3081 (6)	17.3463 (3), 17.3463 (3), 19.8722 (5)	17.7967 (6), 17.7967 (6), 19.2988 (9)	17.7012 (4), 17.7012 (4), 20.5023 (8)	9.9896 (5), 7.2980 (3), 20.0687 (10)	5.2711 (7), 14.3697 (17), 23.766 (3)
α, β, γ (°)	90, 123.487 (5), 90	90, 90, 90	90, 90, 90	90, 90, 90	90, 90, 90	90, 90.958 (2), 90	90, 90, 90
V (Å^3)	6383.4 (5)	5533.5 (3)	5979.4 (3)	6112.4 (5)	6424.0 (4)	1462.89 (12)	1800.1 (4)
Z	6	4	4	4	4	4	4
μ (mm^{-1})	3.14	6.04	5.60	5.47	5.21	5.72	4.66
Crystal size (mm)	0.30 × 0.10 × 0.10	0.07 × 0.07 × 0.06	0.30 × 0.20 × 0.20	0.12 × 0.10 × 0.08	0.16 × 0.06 × 0.02	0.10 × 0.05 × 0.05	0.11 × 0.08 × 0.08
Diffractometer	New Xcalibur, AtlasS2	Bruker D8 Venture	New Xcalibur, AtlasS2	Bruker D8 Venture	Bruker D8 Venture	Bruker D8 Venture	Bruker D8 Venture

		diffractometer		diffractometer	diffractometer	diffractometer	diffractometer
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.927, 1.000	0.639, 0.746	0.933, 1.000	0.540, 0.746	0.568, 0.746	0.606, 0.746	0.582, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22785, 6064, 5445	73022, 4601, 4149	12871, 2839, 2585	46730, 4683, 4011	33846, 4515, 3719	26748, 4490, 3804	14513, 2850, 2327
R_{int}	0.021	0.036	0.024	0.051	0.031	0.042	0.102
θ values (°)	θ_{max} = 25.7, θ_{min} = 2.5	θ_{max} = 31.5, θ_{min} = 2.4	θ_{max} = 25.7, θ_{min} = 2.4	θ_{max} = 30.5, θ_{min} = 2.3	θ_{max} = 29.6, θ_{min} = 1.5	θ_{max} = 30.6, θ_{min} = 2.0	θ_{max} = 24.4, θ_{min} = 2.2
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.610	0.735	0.610	0.715	0.695	0.716	0.582
Range of *h*, *k*, *l*	*h* = -38→39, *k* = -9→6, *l* = -36→33	*h* = -24→24, *k* = -24→24, *l* = -28→28	*h* = -21→17, *k* = -21→17, *l* = -23→24	*h* = -25→25, *k* = -25→25, *l* = -26→27	*h* = -21→24, *k* = -21→24, *l* = -27→28	*h* = -14→14, *k* = -10→10, *l* = -28→28	*h* = -6→5, *k* = -16→16, *l* = -27→27
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.079, 1.05	0.026, 0.060, 1.08	0.062, 0.119, 1.16	0.033, 0.088, 1.02	0.035, 0.089, 1.18	0.052, 0.124, 1.17	0.041, 0.088, 0.95
No. of reflections	6064	4601	2839	4683	4515	4490	2850
No. of parameters	359	172	181	182	190	181	208

No. of restraints	0	0	0	0	0	0	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.0252P)^2 + 47.3496P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0199P)^2 + 22.4482P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + 259.3857P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 25.9649P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0223P)^2 + 58.3205P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0284P)^2 + 18.7285P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2)]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.88, -1.82	2.14, -1.36	2.72, -3.04	2.78, -1.21	1.74, -0.88	3.79, -1.62	0.55, -0.57
Absolute structure	–	?	?	?	?	–	Flack x determined using 780 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	–	?	?	?	?	–	0.02 (5)

Computer programs: *CrysAlis PRO* 1.171.38.41 (Rigaku OD, 2015), *APEX3* (Bruker-AXS, 2016), *SAINT* (Bruker-AXS, 2016), *SHELXS2014* (Sheldrick, 2014), *SHELXT* 2014/5 (Sheldrick, 2014), *SHELXL2014* (Sheldrick, 2014), *SHELXL2017*/1 (Sheldrick, 2017), ShelXle (Hübschle, 2011), CIFTAB-2014 (Sheldrick, 2014).

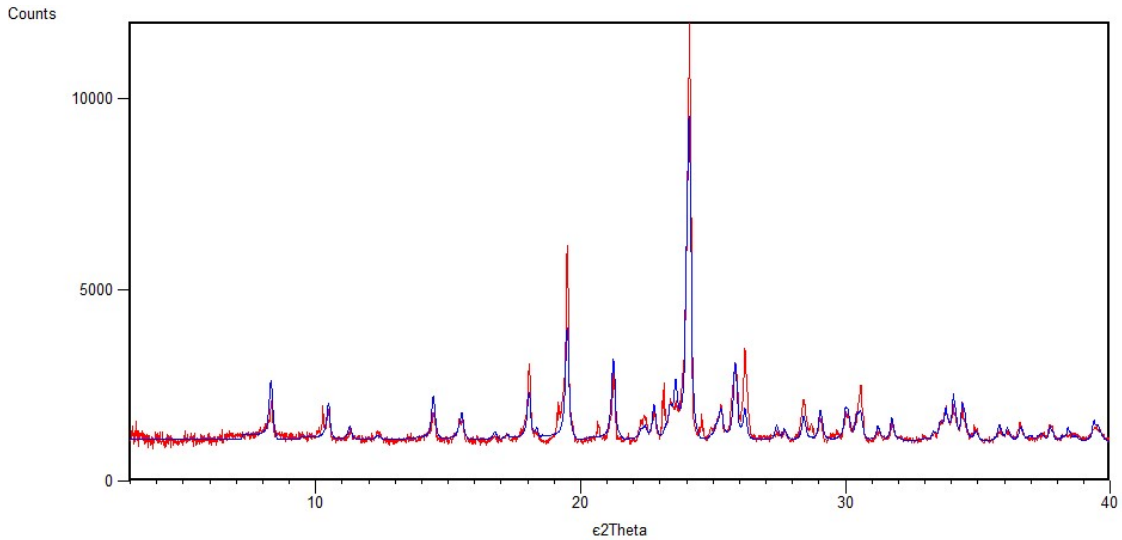


Figure 1S. Calculated and experimental PXRD patterns for **1**

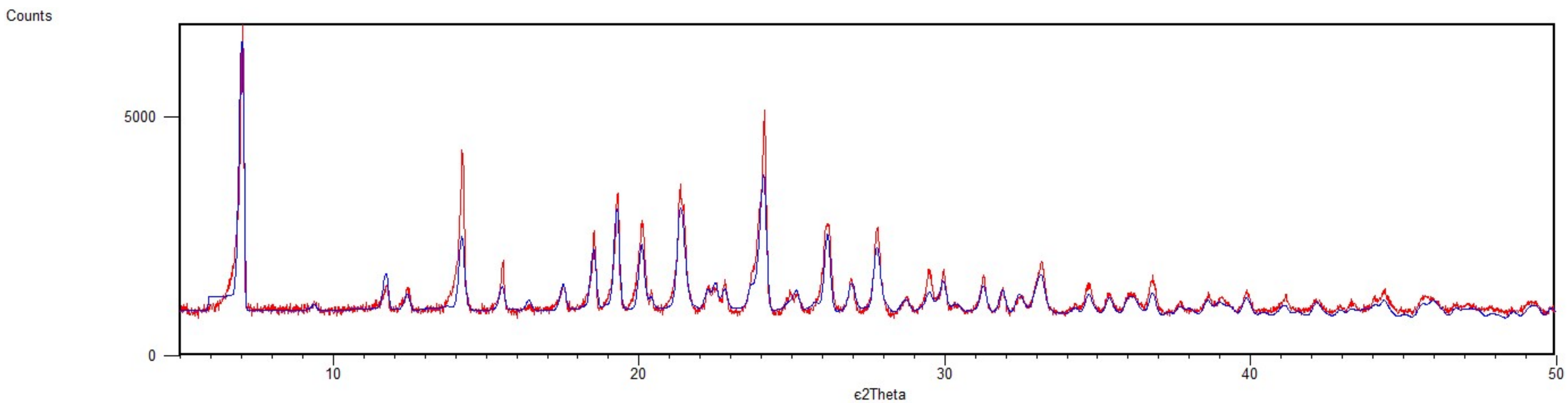


Figure 2S. Calculated and experimental PXRD patterns for **2**

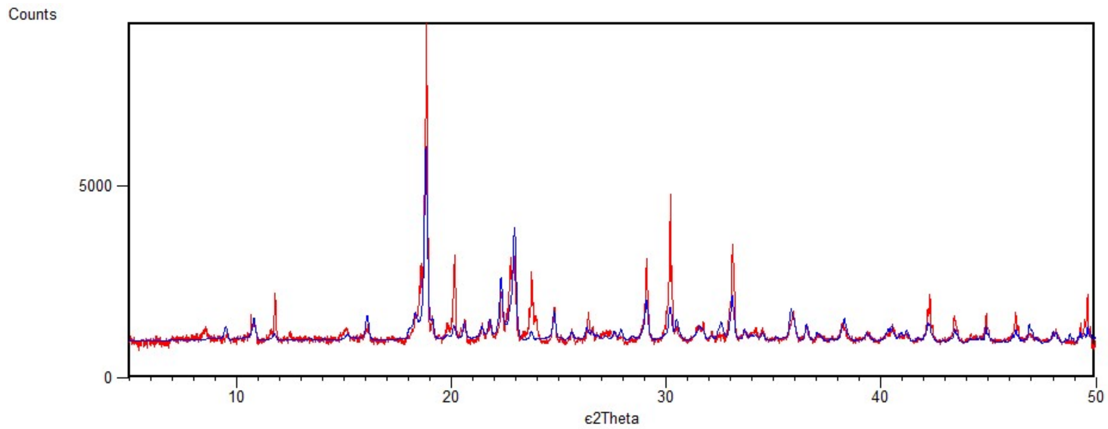


Figure 3S. Calculated and experimental PXRD patterns for **3**

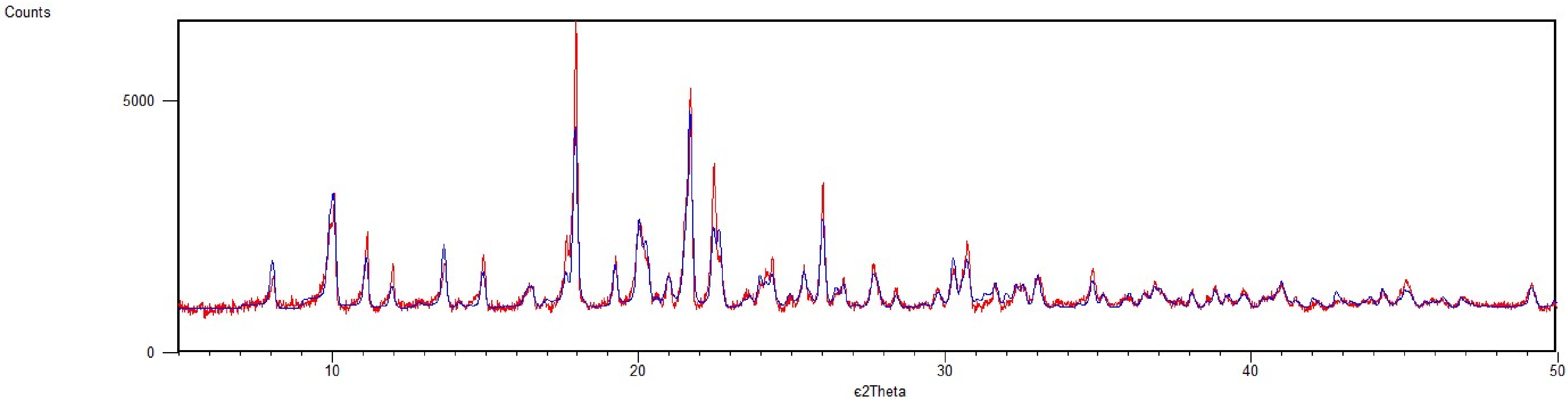


Figure 4S. Calculated and experimental PXRD patterns for **5**

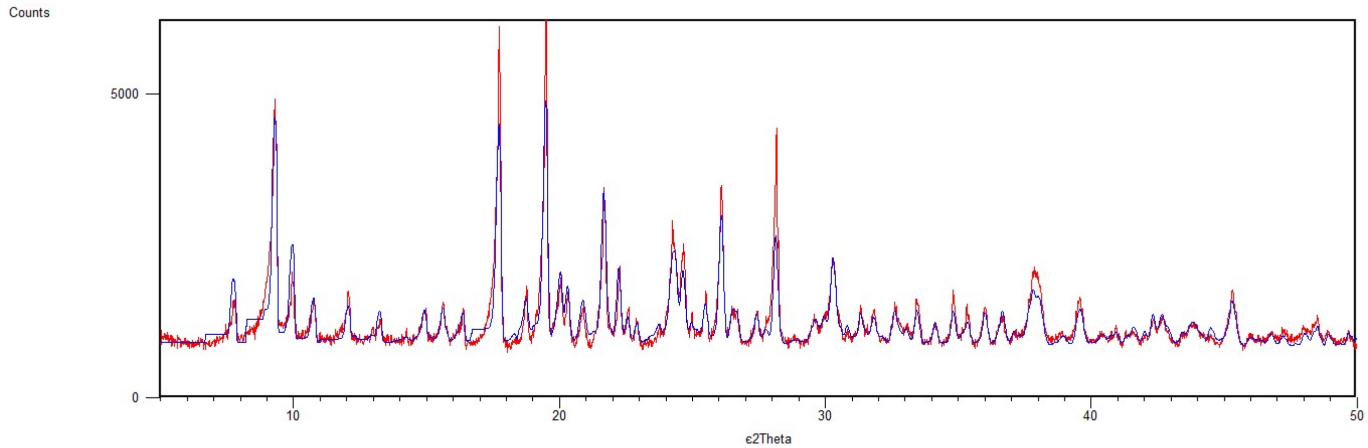


Figure 5S. Calculated and experimental PXRD patterns for **6**

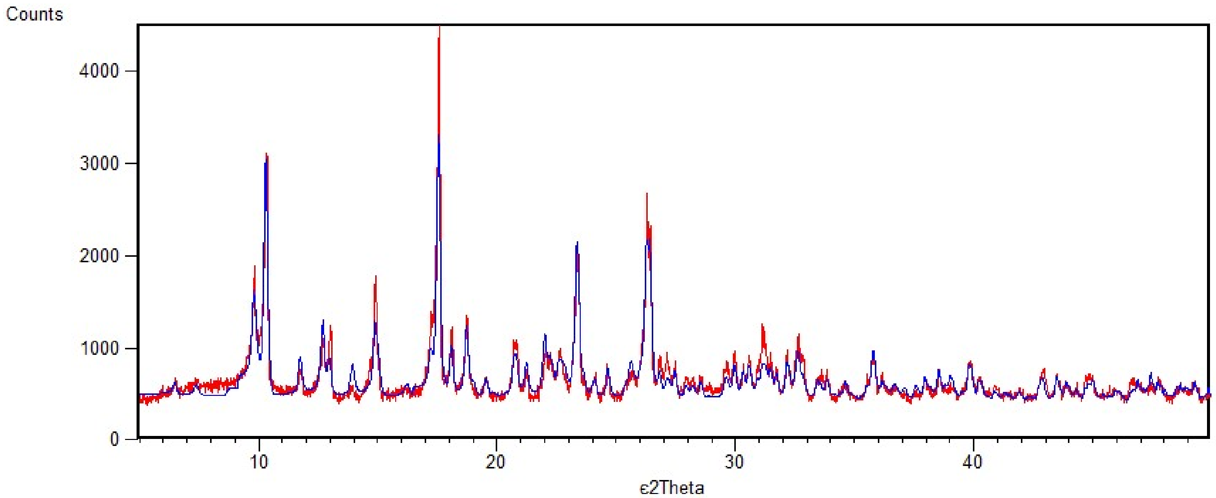


Figure 6S. Calculated and experimental PXRD patterns for **7**

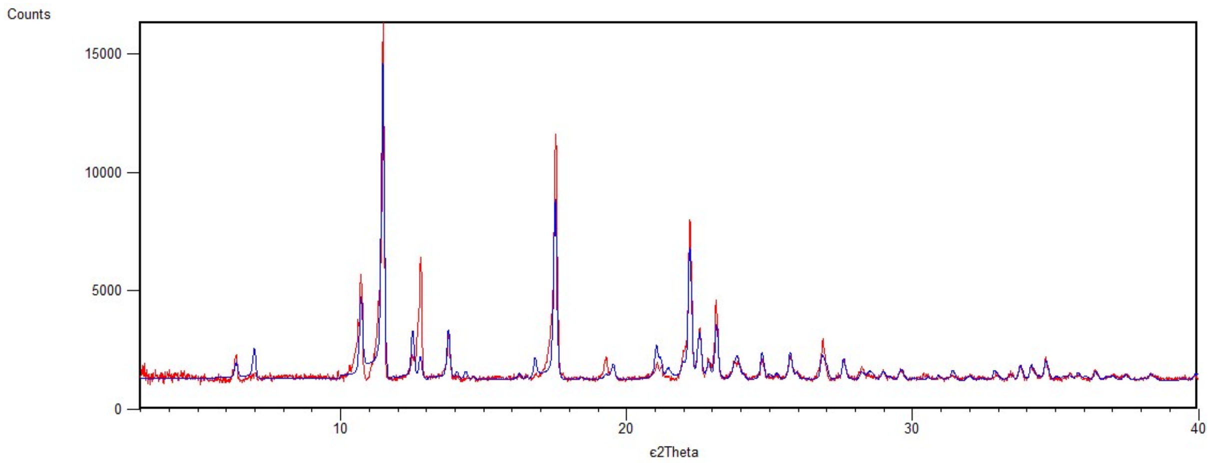


Figure 7S. Calculated and experimental PXRD patterns for **8**

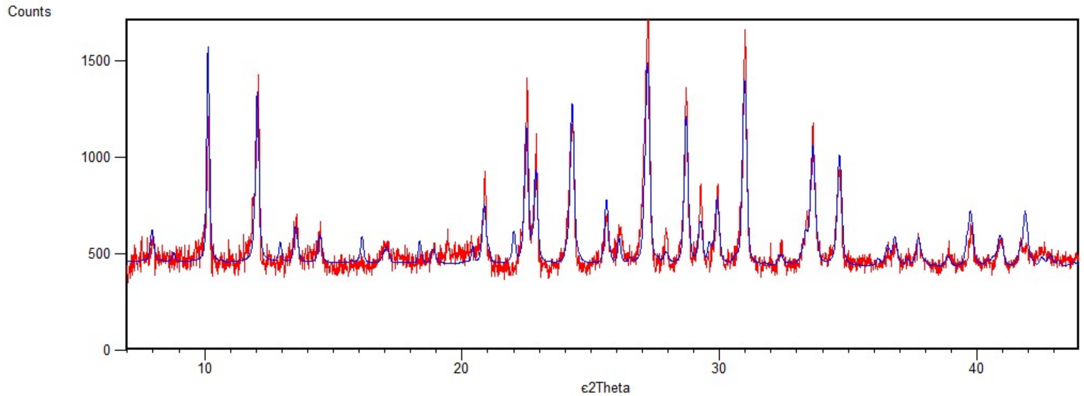


Figure 8S. Calculated and experimental PXRD patterns for **9**

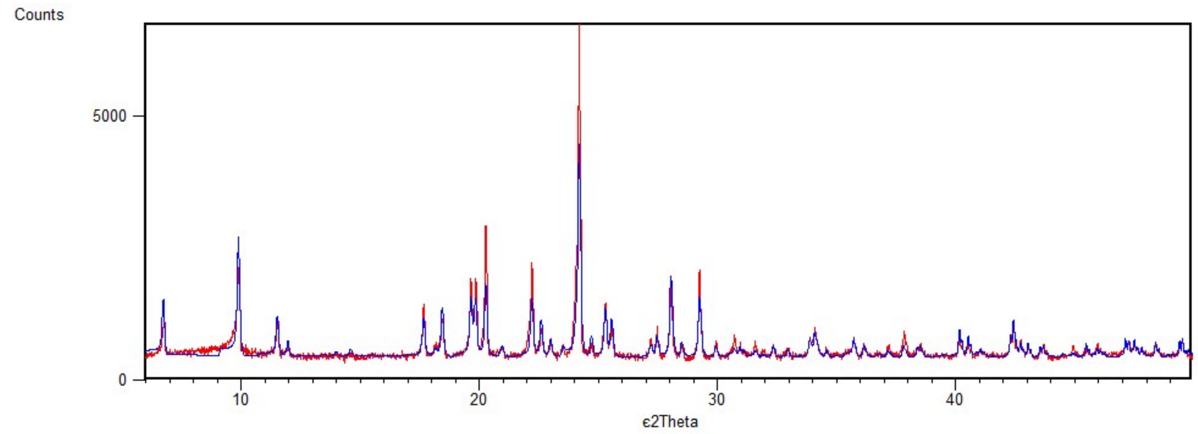


Figure 9S. Calculated and experimental PXRD patterns for **11**

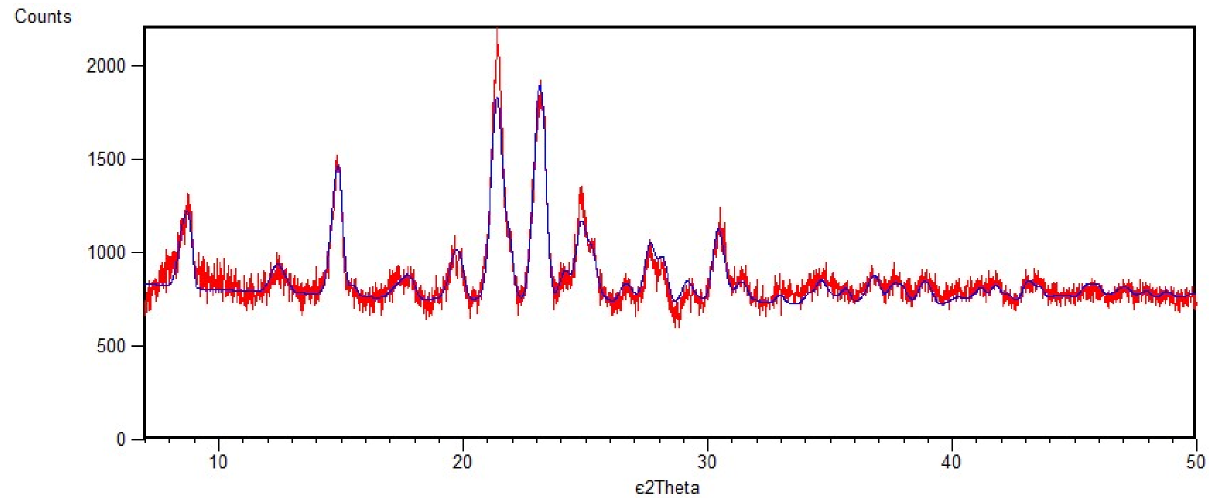
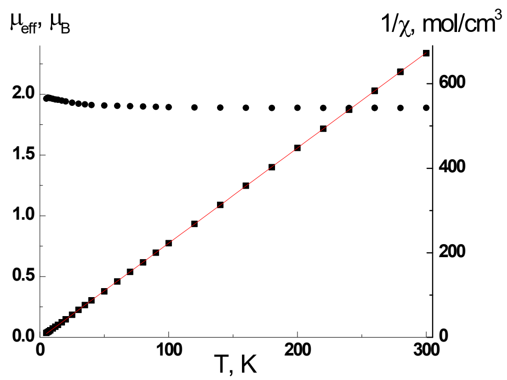
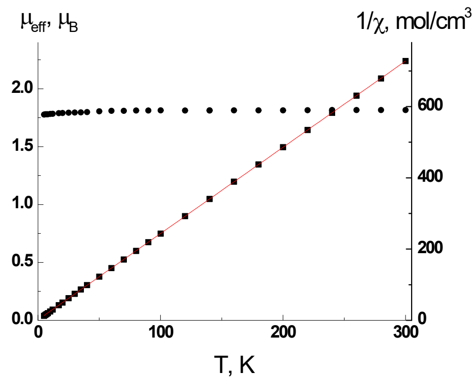


Figure 10S. Calculated and experimental PXRD patterns for **13**

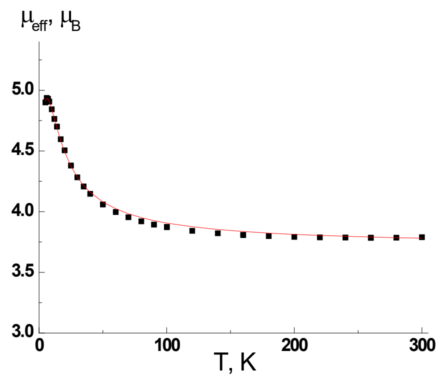


a

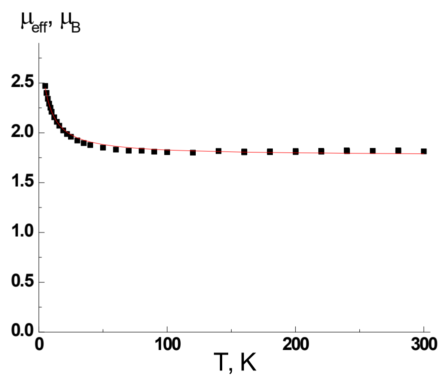


b

Figure 11S. Temperature dependencies of μ_{eff} (●) and $1/\chi$ (■) for the complexes **1** (a) and **2** (b). Solid lines are theoretical curves.



a



b

Figure 12S. Temperature dependencies of μ_{eff} for the complexes **11** (a) and **13** (b). Solid lines are theoretical curves.

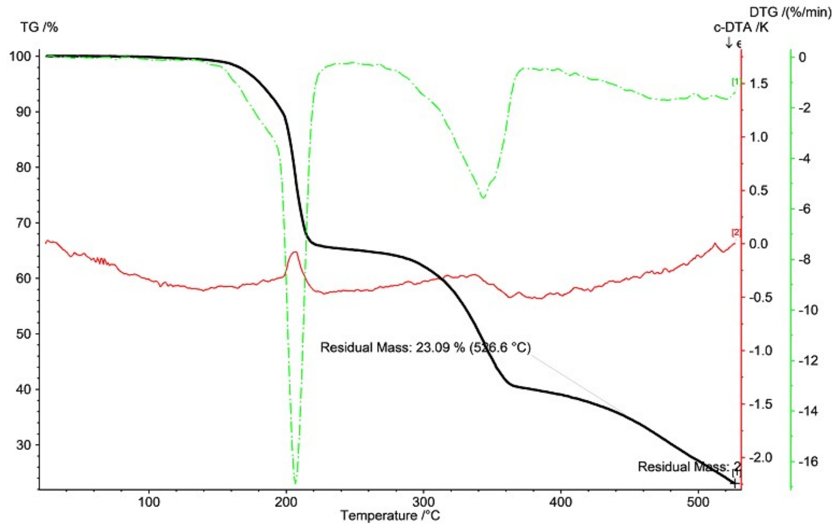


Figure 13S. TGA data for **2**

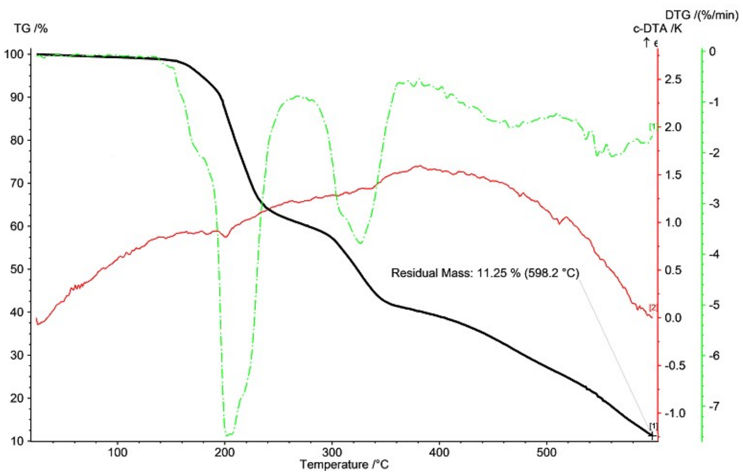


Figure 14S. TGA data for **3**

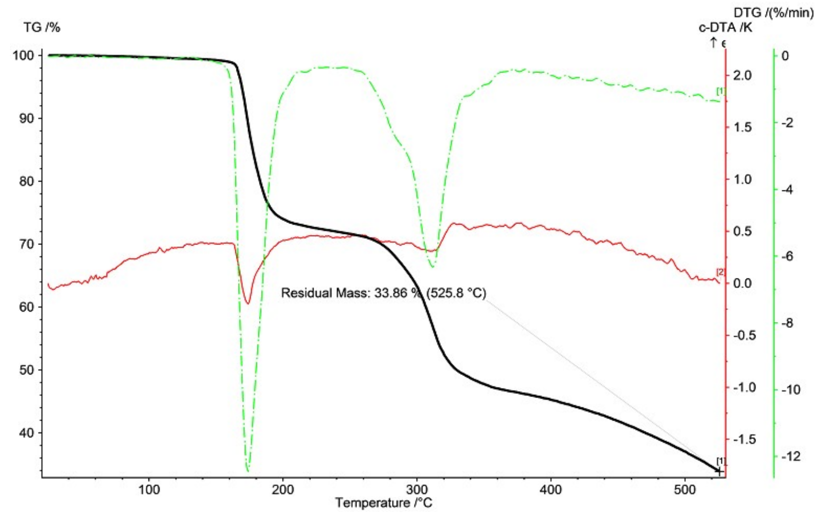


Figure 15S. TGA data for **5**

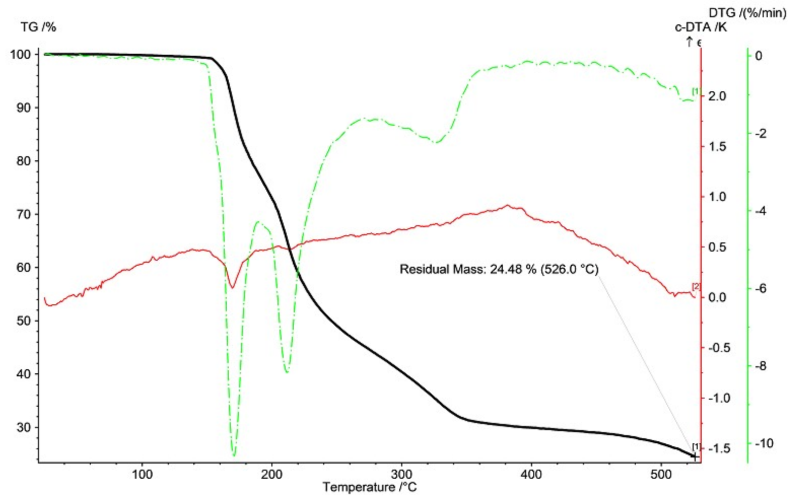


Figure 16S. TGA data for **6**

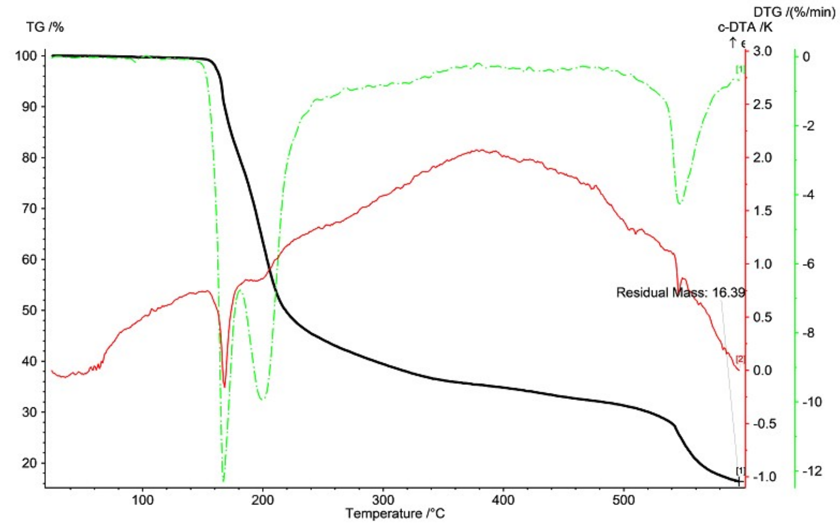


Figure 18S. TGA data for **8**

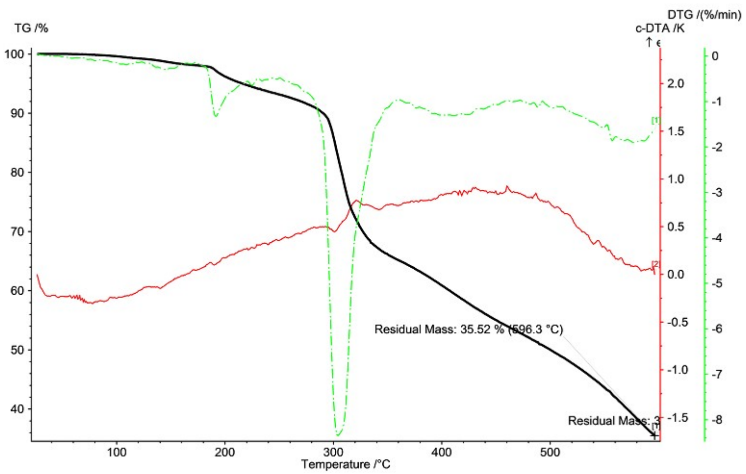


Figure 19S. TGA data for **9**

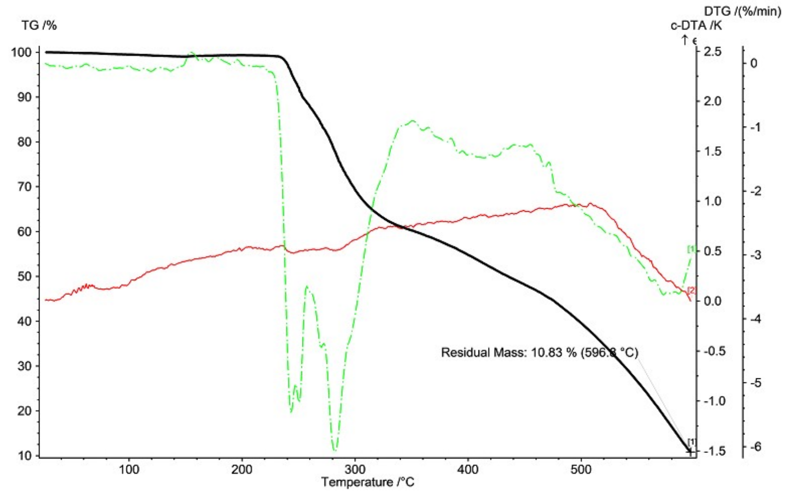


Figure 20S. TGA data for **11**

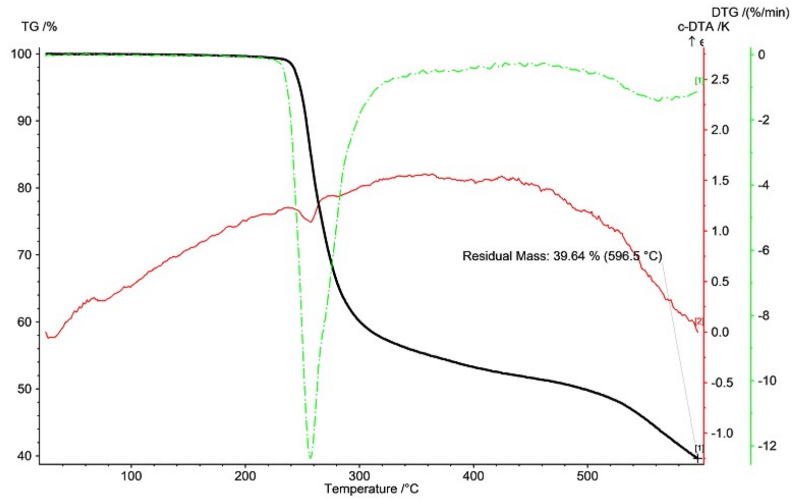


Figure 21S. TGA data for **12**

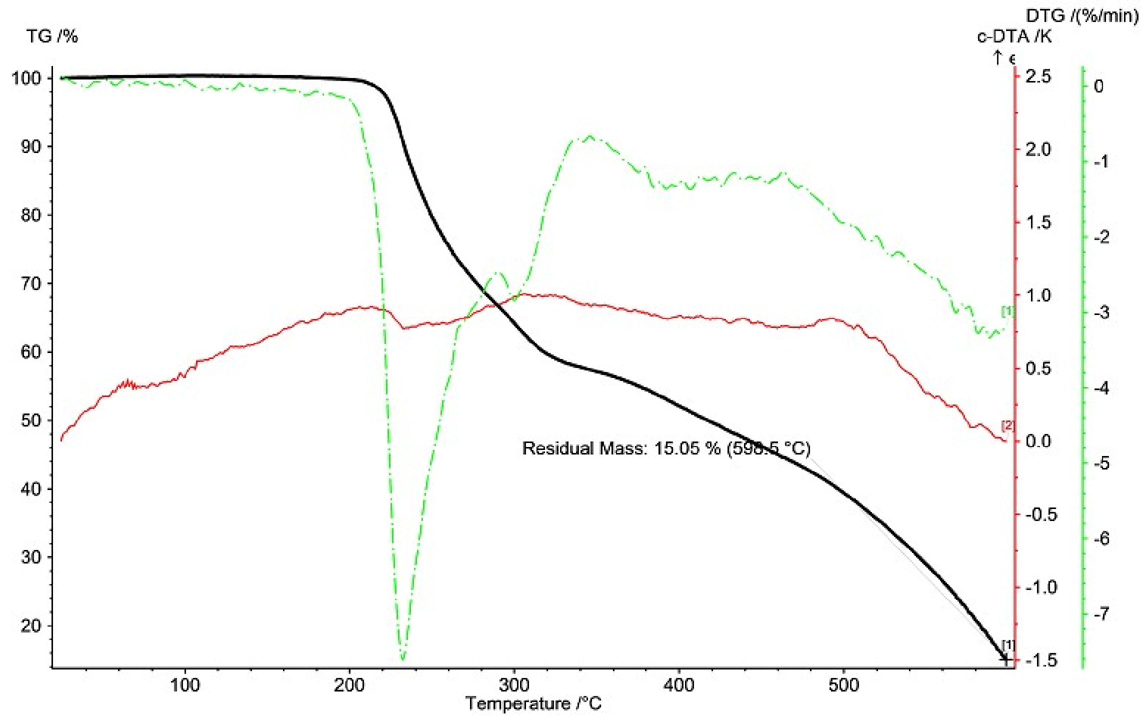


Figure 22S. TGA data for **13**