SUPPLEMENTARY MATERIALS

Thiocyanate copper complexes with pyrazole–derived ligands – Synthesis, crystal structures, DFT calculations and magnetic properties

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Schemes:

Scheme S1. Possible coordination modes of thiocyanate ligand.

Tables:

Figures:

Scheme S1. Possible coordination modes of thiocyanate ligand.

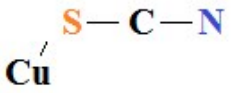
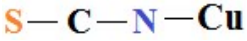
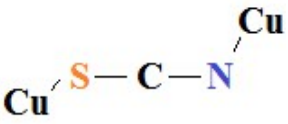
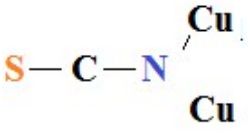
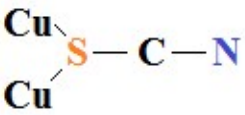
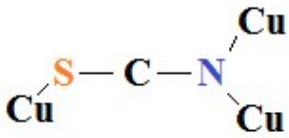
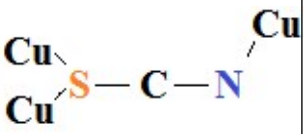
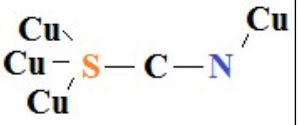
			
S–coordination	**N–coordination**	**$\mu_{-1,3}$ – SCN**	**$\mu_{-1,1}$ – NCS**
			
$\mu_{-1,1}$ – SCN	**$\mu_{-1,1,3}$ – NCS**	**$\mu_{-1,1,3}$ – SCN**	**$\mu_{-1,1,1,3}$ – SCN**

Table S1. Short intra– and intermolecular contacts detected in structures **1**–**4**.

D—H•••A	D—H	H•••A	D•••A [Å]	D—H•••A [°]
1				
O(1)–H(1O)•••S(99)	1.05	2.49	3.4022(17)	143.9
N(2)–H(2A)•••O(1)	0.86	2.39	3.148(3)	147.2
N(2)–H(2A)•••N(99)	0.86	2.44	2.893(3)	113.2
2				
O(1)–H(1)•••S(97)	0.82	2.75	3.484(3)	149.7
N(2)–H(2)•••S(97)	0.86	2.54	3.395(3)	170.6
N(4)–H(4)•••O(1)	0.86	2.14	2.892(3)	146.2
N(4)–H(4)•••N(98)	0.86	2.47	2.910(3)	112.2
N(6)–H(6A)•••O(1)#1	0.86	2.43	3.102(3)	135.7
3				
C(4)–H(4A)•••S(98)#2	0.97	2.84	3.748(4)	156.7
C(8)–H(8B)•••N(99)	0.96	2.52	3.336(7)	143.2
C(10)–H(10B)•••N(98)	0.96	2.57	3.282(7)	131.0
4				
C(9)–H(9)•••S(98)#3	0.93	2.79	3.720(3)	175.3
C(11)–H(11)•••S(99)#4	0.93	2.85	3.681(3)	149.2

Symmetry transformations used to generate equivalent atoms: #1:1–x,1–y,1–z; #2:–x,–1/2+y,1/2–z; #3: x,1/2–y,–1/2+z; #4:–x,1–y,–z

Table S2. The selected bond lengths (Å) and angles (°) for **1.**

Bond lengths [Å]		Bond angles [°]	
Cu(1)–N(1)	2.015(2)	N(1)–Cu(1)–N(1)#a	180.00(11)
Cu(1)–N(99)	1.960(2)	N(1)–Cu(1)–N(99)	90.08(9)
Cu(1)–S(99)#a	2.998(2)	N(1)–Cu(1)–N(99)#a	89.92(9)
C(99)–N(99)	1.156(3)	N(99)–Cu(1)–N(99)#a	180.00(13)
C(99)–S(99)	1.628(3)	C(99)–N(99)–Cu(1)	166.7(2)
		C(99a)–S(99a)–Cu(1)	92.56(1)°
		N(99)–C(99)–S(99)	179.1(3)

Symmetry transformations used to generate equivalent atoms: #a: –x,–y+1,–z

Table S3. The selected bond lengths (Å) and angles (°) for **2.**

Bond lengths [Å]		Bond angles [°]	
Cu(1)–N(1)	1.971(2)	N(1)–Cu(1)–N(3)	176.34(9)
Cu(1)–N(3)	1.983(2)	N(1)–Cu(1)–N(98)	88.93(10)
Cu(1)–N(98)	1.980(2)	N(1)–Cu(1)–N(99)#b	91.20(10)
Cu(1)–N(99)#b	1.970(2)	N(1)–Cu(1)–S(99)	88.62(7)
Cu(1)–S(99)	2.7853(9)	N(3)–Cu(1)–N(98)	90.95(10)
Cu(2)–N(5)	2.009(2)	N(3)–Cu(1)–N(99)#b	90.79(10)
Cu(2)–N(5)#c	2.009(2)	N(3)–Cu(1)–S(99)	87.92(7)
Cu(2)–N(97)	1.950(3)	N(98)–Cu(1)–S(99)	104.44(7)
Cu(2)–N(97)#c	1.950(3)	N(99)#1–Cu(1)–N(98)	148.84(10)
Cu(2)–S(98)	2.9705(8)	N(99)#1–Cu(1)–S(99)	106.71(7)
Cu(2)–S(98)#c	2.9705(8)	N(5)#2–Cu(2)–N(5)	180.00(1)
C(97)–N(97)	1.147(3)	N(97)–Cu(2)–N(5)	89.54(10)
C(97)–S(97)	1.627(3)	N(97)–Cu(2)–N(5)#2	89.54(10)
C(98)–N(98)	1.151(3)	N(97)#2–Cu(2)–N(5)	89.54(10
C(98)–S(98)	1.623(3)	N(97)#2–Cu(2)–N(5)#c	90.46(10)
C(99)–N(99)	1.159(3)	N(97)–Cu(2)–N(97)#c	180.00(11)
C(99)–S(99)	1.630(3)	N(97)–Cu(2)–S(98)	91.25(9)
		S(98)–Cu(2)–S(98)#c	180.00(2)

Symmetry transformations used to generate equivalent atoms: #b: –x,–y+2,–z; #c: –x+1,–y+1,–z+1

Table S4. The selected bond lengths (Å) and angles (°) for **3.**

Bond lengths [Å]		Bond angles [°]	
Cu(1)–N(1)	2.046(4)	N(1)–Cu(1)–N(3)	86.97(14)
Cu(1)–N(3)	2.067(3)	N(1)–Cu(1)–N(97)	93.85(15)
Cu(1)–N(97)	2.130(4)	N(1)–Cu(1)–N(98)	163.51(16)
Cu(1)–N(98)	1.959(4)	N(1)–Cu(1)–N(99)	90.73(16)
Cu(1)–N(99)	1.983(4)	N(3)–Cu(1)–N(97)	92.94(15)
Cu(2)–N(5)	2.099(4)	N(3)–Cu(1)–N(98)	87.88(16)
Cu(2)–N(7)	2.054(4)	N(3)–Cu(1)–N(99)	164.44(15)
Cu(2)–S(97)	2.2752(15)	N(97)–Cu(1)–N(98)	102.05(16)
Cu(2)–S(99)	2.4564(14)	N(97)–Cu(1)–N(99)	102.57(15)
		N(98)–Cu(1)–N(99)	90.03(17)
		N(5)–Cu(2)–N(7)	90.85(14)
		N(5)–Cu(2)–S(97)	120.18(11)
		N(5)–Cu(2)–S(99)	100.63(11)
		N(7)–Cu(2)–S(97)	118.15(13)
		N(7)–Cu(2)–S(99)	115.54(11)
		S(97)–Cu(2)–S(99)	109.50(5)
		C(97)–N(97)–Cu(1)	171.1(4)
		C(98)–N(98)–Cu(1)	174.0(4)
		C(99)–N(99)–Cu(1)	174.1(4)
		C(97)#e–S(97)–Cu(2)	95.55(17)
		C(99)–S(99)–Cu(2)	111.40(17)
		N(97)–C(97)–S(97)#d	178.5(4)
		N(98)–C(98)–S(98)	179.3(4)
		N(99)–C(99)–S(99)	178.8(4)

Symmetry transformations used to generate equivalent atoms: #d: x,y+1,z; #e: x,y–1,z

Table S5. The selected bond lengths (Å) and angles (°) for **4**.

Bond lengths [Å]		Bond angles [°]	
Cu(1)–N(1)	2.029(2)	N(1)–Cu(1)–N(3)	78.06(8)
Cu(1)–N(3)	1.9562(19)	N(1)–Cu(1)–N(5)	151.24(8)
Cu(1)–N(5)	2.080(2)	N(1)–Cu(1)–N(98)	107.25(8)
Cu(1)–N(98)	2.134(2)	N(1)–Cu(1)–N(99)	96.87(9)
Cu(1)–N(99)	1.911(2)	N(3)–Cu(1)–N(5)	77.74(8)
C(98)–N(98)	1.150(3)	N(3)–Cu(1)–N(98)	95.80(9)
C(98)–S(98)	1.634(3)	N(3)–Cu(1)–N(99)	165.78(10)
C(99)–N(99)	1.151(3)	N(5)–Cu(1)–N(98)	90.47(9)
C(99)–S(99)	1.614(3)	N(5)–Cu(1)–N(99)	102.87(9)
		N(98)–Cu(1)–N(99)	98.40(10)
		N(2)–N(1)–Cu(1)	112.78(14)
		N(4)–N(5)–Cu(1)	110.54(15)
		C(1)–N(1)–Cu(1)	141.84(19)
		C(4)–N(3)–Cu(1)	120.19(15)
		C(8)–N(3)–Cu(1)	119.88(17)
		C(11)–N(5)–Cu(1)	141.55(18)
		C(98)–N(98)–Cu(1)	172.9(2)
		C(99)–N(99)–Cu(1)	152.0(2)

Table S6. Selected structural data for copper(II) coordination polymers incorporating thiocyanate bridge.

Compound	Bond lengths [Å]					Bond angles [°]			Cu•••Cu [Å]	Ref.
	$Cu–N_L$	$Cu–N_{NCS}$	$Cu–S_{NCS}$	$N–C_{NCS}$	$C–S_{NCS}$	N–C–S	Cu–N–CS	Cu–S–CN		
double μ$_{1,3}$–NCS										
$[Cu(py)_2(NCS)_2]_n$	2.049(2) 2.055(2)	1.936 (2) 1.932(2)	3.045 (2) 3.085(2)	1.156(3) 1.155(3)	1.628(2) 1.628(2)	179.1(2) 179.2(2)	167.8(1) 169.3(2)	93.2(7) 92.1(8)	5.6477(4)	34
$[Cu(NCS)_2(hmtpo)(H_2O)]_2$	2.074(2)	1.938(3)	2.959(1)	1.150(4)	1.643(3)	179.4(3)	163.1(3)	102.6(1)	5.4991(1)	35
$[Cu(meimi)_2(NCS)_2]_n$	2.013(2)	1.963 (2)	3.221 (1)	1.154 (4)	1.624 (3)	178.8 (3)	167.8 (2)	91.5(2)	5.720(1)	36
$[Cu(im)_2(NCS)_2]$	2.033(2)	1.975(2)	3.135(52)	1.164(3)	1.646(3)	176.8(2)	160.96(19)	93.1(3)	5.720(1)	37
$[Cu(im)_2(NCS)_2]_n$	2.011(2)	1.966(2)	3.1141(6)	1.155(3)	1.633(8)	177.0(8)	161.2(1)	93.1(5)	5.722(4)	38
$[Cu(bpm)(NCS)_2]_n$	2.009(6)	1.941(6)	3.174(2)	1.412(9)	1.638(6)	179.6(7)	165.0(6)	83.1(2)	5.921(2)	39
$[Cu(apo)(NCS)_2]_n$	2.083(2) 1.999(2)	1.934(2)	2.952(1)	1.150(1)	1.643(2)	178.2(3)	173.4(1)	98.0(7)	5.573(1)	36
$[Cu(bipy)(NCS)_2]\}$	1.996(8)	2.012(7)	3.239(4)	1.056(7)	1.674(7)	167.9(10)	165.1(3)	104.7(3)	6.113(2)	41
$[Cu(pyim)(NCS)_2]_n$	2.001(11) 2.014(9)	1.987(10)	3.171(3)	1.159(13)	1.639(15)	178.3(11)	168.3(9)	104.2(5)	6.079(11)	38
single μ$_{1,3}$–NCS										
$[Cu(tmeda)(NCS)_2]_n$	2.071(2) 2.039(2)	1.982(2)	2.825(4)	1.635(3) 1.618(3)	1.166(4) 1.168(4)	178.4(2)	153.2(2)	109.00(9)	5.580(1)	42
$[Cu(detam)(NCS)_2]_n$	1.974 (2) 2.090 (2)	2.8240(7)	2.8240(7)	1.628(2)	1.157(3)	178.8(2)	172.7(2)	100.38(8)	5.8539(5)	43
$[Cu(dpk{\cdot}CH_3OH)(NCS)_2]_n$	2.026(5) 2.032(2)	1.969(3)	2.837(1)	1.145(4)	1.637(3)	179.1(3)	164.4(3)	100.6(1)	5.994(1)	44
$[Cu(pyoxaz)(NCS)_2]_n$	2.048(3) 2.020(3)	1.959(3).	2.271(1)	1.159(5)	1.621(4)	178.5(4)	146.5(3)	97.6(1)	5.599(6)	45
$\{[Cu_2(bpzm)_2(SCN)_4]\}_n$	1.998(2) 2.010(2) 2.003(2) 2.006(2) 2.000(2) 2.013(2) 1.995(2) 2.004(2)	1.945(2); 1.956(3)	2.7387(9) 2.7286(8)	1.138(4) 1.142(4) 1.148(4) 1.150(3)	1.630(3) 1.636(3) 1.637(3) 1.635(3)	179.5(3) 178.7(3)	168.0(3) 170.1(2)	91.2(1) 94.1(1)	5.6043(5) 5.435(5)	13
$[Cu(btb)(NCS)_2]_n$	1.997(1)	1.966(2)	2.9878(1)	1.159(2)	1.625(2)	178.1(2)	157.8(2)	105.5(4)	6.3634(9)	46
$[Cu(isn)_2(NCS)_2]_n$	2.044(1)	1.950(1)	2.9498(4)	1.153(2)	1.628(1)	179.1(1)	159.2(1)	102.0(1)	6.168(9)	47
$[Cu(dmtam)\ (NCS)_2]_n$	1.986 (4) 2.067 (4)	1.961 (4)	2.8386(17)	1.139(9)	1.649(7)	178.6(6)	160.8(5)	91.0(2)	5.222(1)	48

$[Cu(pytr)(NCS)_2]_n$	2.060(4) 1.991(4)	1.968(5)	2.671(2)	1.150(7)	1.641(5)	179.4(5)	170.1(4)	93.2(2)	5.546(1)	49
$[Cu_2(tacte)_2(NCS)_4]_n$	1.935(4) 2.037(4) 2.032(4) 1.937(4) 2.034(5) 2.042(5)	2.306(5)	2.768(2)	1.129(8)	1.632(6)	178.6(6)	138.8(5)	103.1(2)	6.633(4)	50
$[Cu(dach)(NCS)_2]_n$	1.998(11) 2.001(11)	1.959(14)	2.769(4)	1.11(2)	1.65(2)	176.7(14)	169.1(13)	90.3(5)	5.270(2)	51
$[Cu(bim)(NCS)_2]_n$	2.0146(14) 2.0032(14)	1.9490(16)	2.6744(6)	1.145(2)	1.6312(18)	178.62(18)	170.47(16)	97.57(7)	5.6744(3)	52
$[Cu(bpy)(NCS)_2]$	2.003(6) 2.010(7) 2.008(7) 2.003(7)	1.956(7) 1.931(8)	2.728(3) 4.629(2)	1.155(11) 1.155(10)	1.645(10) 1.604(9)	176.8(8) 178.6(8) 178.4(8) 178.3(9)	163.6(8) 168.3(8) 164.8(8) 169.0(7)	97.9(3) 104.5(4)	5.909(2) 6.103(2)	53
$[Cu(4–apy)_2(SCN)_2]_n$	2.023(2) 2.021(2)	1.943(3)	2.867(1)	1.144(4)	1.630(3)	179.0(3)	168.4(4)	87.0(2)	5.495(1)	54
$[Cu(ambzim)(SCN)_2]_n$	1.975(3) 2.025(4)	1.951(4)	2.9521(13)	1.155(6)	1.635(5)	178.4(4)	168.5(4)	93.3(1)	5.540	54
$[Cu(hambi)(NCS)_2]_n$	1.970 (4) 2.022 (4)	1.935(4)	2.942(1)	1.154(6)	1.625(6)	178.9 (5)	169.2(4)	87.2(2)	5.523(2)	55

Table S7. Structural parameters of complexes $[CuL(SCN)_2]$, where L represents a tridentate N–donor ligand

Compound	**Geometry**	**τ**	**Bond lengths [Å]**					**Bond angles [°]**			**Ref.**
			$Cu–N_L$	**$Cu–N_{NCS}$**	**$Cu–S_{NCS}$**	**$N–C_{NCS}$**	**$C–S_{NCS}$**	**N–C–S**	**Cu–N–CS**	**Cu–S–CN**	
					N–coordinated thiocyanate ion						
$[Cu(NCS)_2(mbpyam)]\cdot 0.5CH_2Cl_2$	SP	0.0	2.039 (4)	1.936 (4)	–	1.162 (7)	1.629 (5)	178.3 (4)	140.7 (3)	–	58
	SP	0.10	1.998 (3) 2.016 (3)	2.199 (3)		1.151 (6)	1.634 (4)	179.4 (4)	160.1 (3)		
			2.009 (3) 2.023 (4) 2.034 (4)	2.196 (3) 1.943 (5)	–	1.157 (6) 1.155 (7)	1.638 (5) 1.614 (5)	178.4 (5) 179.2 (4)	151.1 (3) 159.9 (3)	–	
$[Cu(L^1)(NCS)_2]$	SP	0.09	2.034(3) 2.024(3)	2.268(4) 1.959(3)	–	1.158(6) 1.150(6)	1.635(5) 1.631(5)	178.9(4) 178.7(4)	170.1(3) 147.1(3)	–	60

			2.010(3)								
[Cu(buterpy)(NCS)$_2$]	SP SP	0.05 0.16	2.045(5) 1.957(4) 2.029(4) 2.053(5) 1.940(4) 2.040(5)	2.105(5) 1.971(5) 2.132(5) 1.930(4)	–	1.167(7) 1.159(7) 1.159(7) 1.157(7)	1.634(6) 1.623(6) 1.656(6) 1.620(6)	178.3(5) 179.2(5) 179.7(5) 178.9(5)	175.2(4) 147.7(4) 176.9(5) 153.9(4)	–	61
[Cu(mpiq)(NCS)$_2$]	SP	0.11	2.0239(12) 2.0218(11) 2.0658(12)	1.9887(13) 2.0624(13)	–	1.1644(19) 1.160(2)	1.6276(16) 1.6257(15)	179.44(14) 178.50(15)	162.18(12) 146.07(13)	–	70
[Cu(bpzeaT)(SCN)$_2$]	SP	0.15	1.942(3) 2.102(3) 2.101(3)	1.956(3) 2.134(4)	–	1.159(5) 1.140(6)	1.618(5) 1.606(4)	177.8(4) 179.5(4)	170.1(4) 172.8(4)	–	73
[Cu(dpymedam)(NCS)$_2$]	SP	0.18	2.053 (4) 1.954 (3) 2.096 (4)	1.921 (4) 2.151 (5)	–	1.117(7) 1.146(7)	1.610(5) 1.593(5)	179.81(5) 178.81(4)	168.02(5) 166.44(4)	–	62
[Cu(bzbedmpza)(NCS)$_2$]	SP	0.26	1.992(5) 2.238(4) 1.990(5)	1.969(4) 1.993(4)	–	1.150(6) 1.146(6)	1.610(5) 1.617(5)	179.5(5) 178.1(5)	155.2(5) 156.5(5)	–	63
[Cu(bdmpzpy)(NCS)$_2$]	SP	0.25	2.0295(10) 2.0689(9) 2.0355(10)	1.9845(11) 2.1225(10)	–	1.1692(17) 1.1637(16)	1.6300(13) 1.6299(12)	179.01(11) 178.67(11)	151.00(10) 176.42(10)	–	64
[Cu(dipyp) (NCS)$_2$]	SP	0.26	2.038 (3) 2.041 (3) 2.071 (3)	2.131 (3) 1.974 (3)	–	1.164(4) 1.149(4)	1.615(3) 1.620(5)	178.2 (3) 179.1 (4)	153.45(3) 177.94(3)	–	66
[Cu(mebedmpza)(NCS)$_2$]	SP	0.26	2.013(3) 2.181(4) 2.013(3)	1.982(3) 1.982(3)	–	1.159(5)	1.623(3)	179.1(3)	166.7(3)	–	63
[Cu(ipracn)(NCS)$_2$]	SP	0.27	2.254(3) 2.102(4) 2.087(3)	1.966(3) 1.952(3)	–	1.150(4) 1.161(4)	1.616(4) 1.608(4)	178.9(4) 178.8(4)	155.9(3) 161.8(3)	–	74
[Cu(dpyetam)(NCS)$_2$]	SP	0.28	2.211 (3) 2.061 (2) 2.222 (3)	1.963 (3) 1.958 (3)	–	1.141(1) 1.141(1)	1.689(2) 1.607(3)	178.14(3) 179.64(3)	167.8(3) 160.5(3)	–	67
[Cu(dpydiam)(NCS)$_2$]	SP	0.28	2.047 (3) 2.013 (3) 2.078 (3)	2.153 (3) 1.955 (3)	–	1.126 (4) 1.151 (4)	1.600 (4) 1.622 (4)	178.9 (4) 179.4 (3)	152.2 (3) 169.4 (3)	–	68
[Cu(dpt)(NCS)$_2$]	SP	0.30	2.037	2.140	–	1.142	1.620	178.4(2)	169.6(4)	–	69

			2.061 2.020	2.037		1.150	1.620	178.9(7)	168.1(2)		
[Cu(tppz)(SCN)$_2$]	SP	0.31	1.946(2) 2.011(3) 2.014(3)	1.907(3) 2.692(3)	–	1.163(4) 1.139(5)	1.612(3) 1.630(4)	178.8(4) 179.3(4)	163.1(3) 115.3(3)	–	16
[Cu(mpipq)(NCS)$_2$]	SP	0.33	2.0269(9) 2.0824(10) 2.0243(10)	2.1074(10) 1.9477(10)	–	1.1637(15) 1.1656(15)	1.6334(12) 1.6315(11)	179.10(12) 178.67(11)	158.65(10) 167.65(10)	–	70
[Cu(me$_3$dpt)(NCS)$_2$]	SP SP/TBY	0.37 0.49	2.026(3) 2.190(3) 1.994(3)	1.994(3) 2.003(3)	–	1.157(4) 1.158(4)	1.627(4) 1.640(4)	178.9(3) 179.0(3)	173.6(3) 171.1(3)	–	9
			2.203(3) 2.028(3) 2.046(3)	2.010(3) 1.992(3)	–	1.166(5) 1.157(4)	1.625(4) 1.640(4)	179.2(3) 178.8(3)	164.4(3) 174.3(3)	–	
[Cu(pyetam)(NCS)$_2$]	SP/TBY	0.48	2.002(6) 2.125(8) 1.994(6)	1.97(2) 2.098(9)	–	1.137(1) 1.140(1)	1.637(9) 1.597(9)	178.41(8) 179.13(8)	175.81(7) 170.38(8)	–	59
[Cu(terpy)(NCS)$_2$]	SP/BPY	0.53	2.021(5) 2.021(5) 1.937(7)	2.020(7)	–	1.157(11)	1.631(8)	178.4(6) 178.4(6)	156.6 (5) 156.6 (5)	–	72
[Cu(bedmpza)(NCS)$_2$]MeOH	BPY	0.76	2.0067(12) 2.1309(12) 2.0140(12)	1.9967(13) 1.9908(13)	–	1.1564(19) 1.1606(19)	1.6277(15) 1.6301(14)	178.61(14) 178.20(14)	164.51(13) 168.22(13)	–	71
S–coordinated thiocyanate ion											
[Cu(L^2)(NCS)$_2$]	SP	0.03	1.993(4) 2.048(4) 1.993(4)	1.951(5)	2.682(1)	1.142(7) 1.177(8)	1.646(6) 1.619(6)	179.47(5) 177.92(5)	159.1(4).	100.5(2).	60
[Cu(apscarb)(NCS)$_2$]	SP	0.18	1.974(3) 1.957(3) 2.011(3)	1.908(3)	2.684(2)	1.271(4) 1.367(4)	1.772(4) 1.740(3)	178.6(4) 177.4(4)	168.8(3)	99.787(2)	75
[Cu(bbp)(NCS)$_2$]MeOH	SP	0.18	1.980(2) 2.156(5) 2.142(4)	1.918(2)	2.5777(17)	1.150(3) 1.177(4)	1.630(3) 1.662(3)	178.7(3) 177.1(3)	163.7(3)	97.29(11)	73
[Cu(pyterpy)(NCS)$_2$]	SP	0.25	2.029 (3) 1.924 (2) 2.029 (3)	1.909 (3)	2.818(4)	1.147(2) 1.139(3)	1.655(2) 1.616(1)	179.0(3) 179.1(3)	166.87(3)	101.13(1)	65

Table S8. NBO atomic spin density [Δ, in e] on selected atoms in the triple state of the **1**. Level of calculations B3LYP–D3/LanL2dz.

	α	β	Δ	Δ^a	Δ^b
Cu1	14.330	13.738	0.592	0.576	0.016
N1	3.738	3.642	0.096	0.098	–0.002
N99	3.894	3.819	0.075	0.077	–0.002
S99	8.096	8.036	0.060	0.046	0.014
N(1A)	3.743	3.644	0.100	0.098	0.002
N(99A)	3.872	3.809	0.064	0.077	–0.013
S(99A)	8.078	8.048	0.030	0.046	–0.016
Cu(1A)	14.330	13.738	0.592	0.576	0.016
N1#	3.743	3.644	0.100	0.098	0.002
N99#	3.872	3.809	0.064	0.077	–0.013
S99#	8.078	8.048	0.030	0.046	–0.016
N(99A)#	3.738	3.642	0.096	0.098	–0.002
S(99A)#	8.096	8.037	0.060	0.046	0.014

[a] NBO atomic spin density on selected atoms in the doublet state of the $[Cu(mpz)_2(NCS)_2]$ monomer. [b] Differences between the values of the Δ and Δ^a.

Table S9. NBO atomic spin density [Δ, in e] on selected atoms in the quartet state of the **2**. Level of calculations B3LYP–D3/LanL2dz.

	α	β	Δ
Cu(1)	14.344	13.750	0.594
Cu(2)	14.332	13.826	0.505
N(1)	3.751	3.648	0.103
N(3)	3.745	3.638	0.107
C(98)	2.883	2.898	–0.015
N(98)	3.885	3.818	0.068
N(99)	3.842	3.760	0.082
S(98)	8.115	7.924	0.191
S(99)	8.110	8.075	0.034
Cu(1B)	14.342	13.730	0.612
N(1B)	3.740	3.640	0.100
N(3B)	3.745	3.634	0.111
N(98B)	3.875	3.813	0.063
N(99B)	3.844	3.767	0.077
S(98B)	8.103	8.062	0.041
S(99B)	8.101	8.059	0.042
N(5)	3.734	3.651	0.083

C(97)	2.911	2.921	–0.010
N(97)	3.882	3.793	0.089
S(97)	8.107	8.049	0.058

Table S10. NBO atomic spin density [Δ, in e] on selected atoms in the triplet state of the **3** and in the doublet state of the **3.** Level of calculations B3LYP–D3/LanL2dz.

	α	β	Δ	Δ^a	Δ^b
Cu(1)	14.376	13.748	0.628	0.621	0.007
N(3)	3.740	3.628	0.112	0.085	0.027
N(1)	3.816	3.758	0.057	0.075	–0.018
N(99)	3.851	3.768	0.083	0.085	–0.002
N(98)	3.799	3.728	0.072	0.037	0.035
S(99)	8.129	8.066	0.063	0.065	–0.002
Cu(2)	14.380	13.716	0.664	0.621	0.043
N(5)	3.725	3.632	0.093	0.085	0.008
C(98)	2.895	2.907	–0.012	–0.010	–0.002
N(7)	3.857	3.770	0.087	0.075	0.012
N(99A)	3.854	3.779	0.075	0.085	–0.010
N(98A)	3.834	3.733	0.101	0.037	0.064
S(97A)	8.131	8.120	0.011	0.065	–0.054

[a] NBO atomic spin density on selected atoms in the doublet state of the [(bdmpzm)$Cu^{II}(SCN)_2(\mu_{1,3}$–SCN)Cu^{I}(bdmpzm)]. [b] Differences between the values of the Δ and Δ^a.

Table S11. NBO atomic spin density [Δ, in e] on selected atoms in the triplet state of the **4** dimer and in the doublet state of the **4**. Level of calculations B3LYP–D3/LanL2dz.

	α	β	Δ	Δ^a	Δ^b
Cu(1)	14.342	13.737	0.604	0.603	0.001
N(1)	3.700	3.640	0.060	0.077	–0.017
N(3)	3.831	3.735	0.096	0.085	0.011
N(5)	3.700	3.647	0.053	0.054	–0.001
N(99)	3.847	3.757	0.090	0.087	0.003
S(99)	8.146	8.065	0.081	0.111	–0.03
C(99)	2.903	2.912	–0.010	–0.015	0.005
Cu(1A)	14.342	13.738	0.604	0.603	0.001
N(1A)	3.700	3.640	0.059	0.077	–0.018
N(3A)	3.831	3.735	0.096	0.085	0.011
N(5A)	3.700	3.647	0.053	0.054	–0.001

N(99A)	3.848	3.757	0.090	0.087	0.003
S(99A)	8.146	8.065	0.081	0.111	–0.03
C(99A)	2.902	2.911	–0.010	–0.015	0.005

Table S12. Selected bond lengths(Å) and angles(°) for complex **1**.

		experimental	monomer	dimer
Distances				
	Cu(1)–N(1)	2.015	2.014	2.017
	Cu(1)–N(99)	1.960	1.985	2.002
	Cu(1)–N(1A)	2.014	2.014	2.003
	Cu(1)–N(99A)	1.959	1.985	2.018
	Cu(1)–Cu(1#)	5.622	-	5.303
Angles				
	Cu(1)–N(1)–N(2)	123.78	118.35	117.22
	Cu(1)–N(99)–C(99)	166.78	150.79	146.99
	Cu(1)–N(1A)–N(2A)	123.78	118.35	119.24
	Cu(1)–N(99A)–C(99A)	166.78	150.80	151.34
	N(1)–Cu(1)– N(99)	90.08	88.51	88.69
	N(1)–Cu(1)– N(99A)	89.92	91.88	90.75
	N(99)–Cu(1)–N(1A)	89.90	91.88	93.01
	N(1A)–Cu(1)–N(99A)	90.10	88.51	88.54
	N(99A)– N(1A)– N(99)–Cu(1)	0.10	4.63	10.21
	N(99)–N(1)– N(99A)–Cu(1)	0.08	4.63	10.16

Table S13. Selected bond lengths(Å) and angles(°) for complex **2**.

		experimental	dimer
Distances			
	Cu(1)–N(1)	1.971	1.972
	Cu(1)–N(3)	1.983	1.972
	Cu(1)–N(98)	1.980	1.990
	Cu(1)–N(99)	1.949	2.091
	Cu(1)–Cu(2)	6.52	5.224
	Cu(1)–Cu(1#)	6.51	5.029
Angles			
	N(1)–Cu(1)–N(3)	176.34	172.04
	N(99)–Cu(1)–N(98)	161.58	148.32
	N(1)–N(98)–N(3)–Cu(1)	2.590	4.64
	N(1)–N(99)–N(3)–Cu(1)	2.59	5.48

Table S14. Selected bond lengths(Å) and angles(°) for complex **3**.

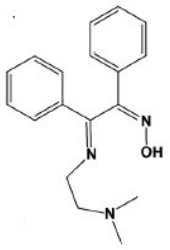
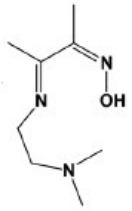
		experimental	monomer	dimer
Distances				
	Cu(1)–Cu(2)	6.17	5.538	5.650
	Cu(1)–N(1)	2.046	2.068	2.275

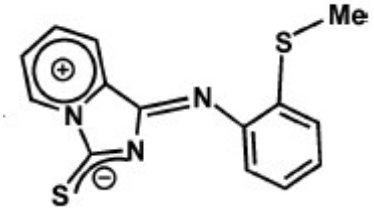
	Cu(1)–N(3)	2.067	2.248	2.048
	Cu(1)–N(97)	2.130	2.015	2.045
	Cu(1)–N(98)	1.959	1.998	1.991
	Cu(1)–N(99)	1.983	2.152	2.041
Angles				
	N(3)–Cu(1)–N(1)	86.97	86.93	86.46
	N(97)–Cu(1)–N(98)	102.05	92.04	153.10
	N(98)–Cu(1)–N(99)	90.03	88.26	90.38
	N(97)–N(98)–N(99)–Cu(1)	44.92	11.88	18.47

Table S15. Selected bond lengths(Å) and angles(°) for complex **4**.

		experimental	monomer	dimer
Distances				
	Cu(1)–N(1)	2.029	2.070	2.087
	Cu(1)–N(3)	1.956	2.040	2.010
	Cu(1)–N(5)	2.080	2.129	2.128
	Cu(1)–N(98)	2.134	2.161	2.134
	Cu(1)–N(99)	1.911	1.923	1.912
	Cu(1)–Cu(1A)	8.47		5.42
Angles				
	N(1)–Cu(1)–N(3)	78.06	77.58	77.88
	N(3)–Cu(1)–N(5)	77.74	76.30	77.03
	N(3)–Cu(1)–N(98)	95.80	85.63	90.01
	N(3)–Cu(1)–N(99)	165.78	162.53	171.55
	N(98)–Cu(1)–N(99)	98.40	111.84	98.40
	N(1)–N(3)–N(5)–Cu(1)	12.72	10.10	12.22

Table S16. Mixed valence Cu(II)/Cu(I) complexes based on the thiocyanato ion.

Compound name	**Ligand**	**Preparation method**	**Reference**
$[Cu^{II}_2(L)_2(NCS)]_2[Cu^{I}(SCN)(\mu_{1,1}\text{-}SCN)(\mu_{1,3}\text{-}SCN)]\}$		$Cu(ClO_4)_2 \cdot 6H_2O$, MeOH, rt	22
$\{[Cu^{II}_2(L)_2][Cu^{I}_4(\mu_{1,3}\text{-}SCN)_4(\mu_{1,1,3}\text{-}SCN)_2]\}_n$		$Cu(CH_3COO)_2$, MeOH, rt	22
$[Cu_2^{I}Cu^{II}(pyz)_2(C_5O_5)_2(H_2O)_2]_n$	pyrazine	$Cu(NO_3)_2 \cdot 3H_2O$, $MeOH/H_2O$, solvatothermal synthesis, 393K	20
$[Cu_8^{I}Cu_2^{II}(CN)_4(NCS)_8(C_6H_8N_2)_7]$	2,6-dimethylpyrazine	CuSCN, MeCN/solvatothermal	92

		synthesis,413K	
$[Cu^{I}_2Cu^{II}(admtrz)_6(SCN)_2](ClO_4)_2$	4-amino-3,5-dimethyl-1,2,4-triazole	$Cu(ClO_4)_2·6H_2O$, EtOH/H_2O/rt	97
$Cu_2(L)(\mu_{-1,3}\text{-}SCN)_2(SCN)]_n$	4¢-(4-pyridyl)-2,2¢:6¢,2¢¢-terpyridine	$CuCl_2·2H_2O$, EtOH, solvatothermal synthesis, 413K	32
$\{[Cu(C_{21}H_{15}N_3)_2][Cu_2(NCS)_4]\}_n$	4'-phenyl-2,2':6',2''-terpyridine	$Cu(CH_3COO)_2·H_2O$, EtOH,solvatothermal synthesis, 473K	93
$\{[Cu(C_{20}H_{14}N_4)_2][Cu_2(NCS)_4]\}_n$	4'-(3-pyridyl)-2,2':6',2''-terpyridine	$Cu(CH_3COO)_2·H_2O$ EtOH,solvatothermal synthesis, 413K	94
$\{[Cu(bpzm)(SCN)][Cu(bpzm)(MeOH)][Cu(SCN)_4]\}_n$	bis(pyrazol-1-yl)methane	$CuCl_2·2H_2O$, MeOH/H_2O,rt	13
$\{[Cu_2(bpzm)_2(\mu\text{-}SCN)(SCN)_3]\}_n$	bis(pyrazol-1-yl)methane	$CuCl_2·2H_2O$, MeOH/H_2O,rt	13
$Cu_2(SCN)_2$(2-PyBIm)(2-PyHBIm)]$_n$	2-(n-pyridyl)benzimidazole	CuSCN, MeCN, solvatothermal synthesis, 443K	96
$[Cu(DMF)_4][Cu(SCN)_4(CN)_2]$	DMF	dissolution of copper, DMF/propanol; synthesis, 373K	23
$\{[KCu^{II}_6(bdap)_6(\mu_{1,3}\text{-}SCN)_3Cu^{I}(NCS)](SCN)_4\}_n$	1,3-bis(amino)-2-propanol	$Cu(NO_3)_2·3H_2O$, EtOH/H_2O, rt	95
$\{[Cu^{II}_2(\mu\text{-}L)(\mu\text{-}H_2O)3H_2O][Cu^{I}\text{-}\mu_{(1,3}\text{-}NCS)_2]\}_n$	imidazolidinyl phenolate Schiff base	$Cu(ClO_4)_2·6H_2O$, MeOH/MeCN, rt	25a
$[(L)Cu_2(SCN)_3]_n$		$Cu(ClO_4)_2·6H_2O$ CH_2Cl_2/MeOH, rt	26
$[Cu^{II}Cu^{I}(L)(\mu\text{-}SCN)(\mu_3\text{-}SCN)]_n$	N′-((pyridin-2-yl)methylene)acetohydrazide)	$Cu(CH_3COO)_2·H_2O$ MeCN/MeOH/H_2O,rt	21
[Cu(NCS)(tpea)][Cu(NCS)$_2$]	tris(2-pyrazolylethyI)amine (tpea)	$CuCl_2·2H_2O$, EtOH/acetone, rt	19
$[Na(Cu^{II}L)_2][Cu^{I}_2(\mu_{1,3}\text{-}NCS)_3]_n$	*N*,*N*-bis(3-ethoxysalicylidenimino)-1,3-diaminopropane	$Cu(CH_3COO)_2·H_2O$ MeOH/H_2O, rt	98
$[\{(Cu^{II}_2L_2)\}\{Cu^{I}_4(\mu_{1,3}\text{-}SCN)_2(\mu_{1,1,3}\text{-}SCN)_4\}]_n$	3-[2-(dimethylamino)ethylimino]butan-2-one oxime	$Cu(ClO_4)_2·6H_2O$, EtOH/H_2O/rt	25b
$[\{(Cu^{II}_2L_2)\}\{Cu^{I}_2(\mu_{1,3}\text{-}SCN)_2(\mu_{1,1,3}\text{-}SCN)_2\}]_n$	3-[2-(diethylamino)ethylimino]butan-2-one oxime	$Cu(ClO_4)_2·6H_2O$, EtOH/H_2O/rt	25b

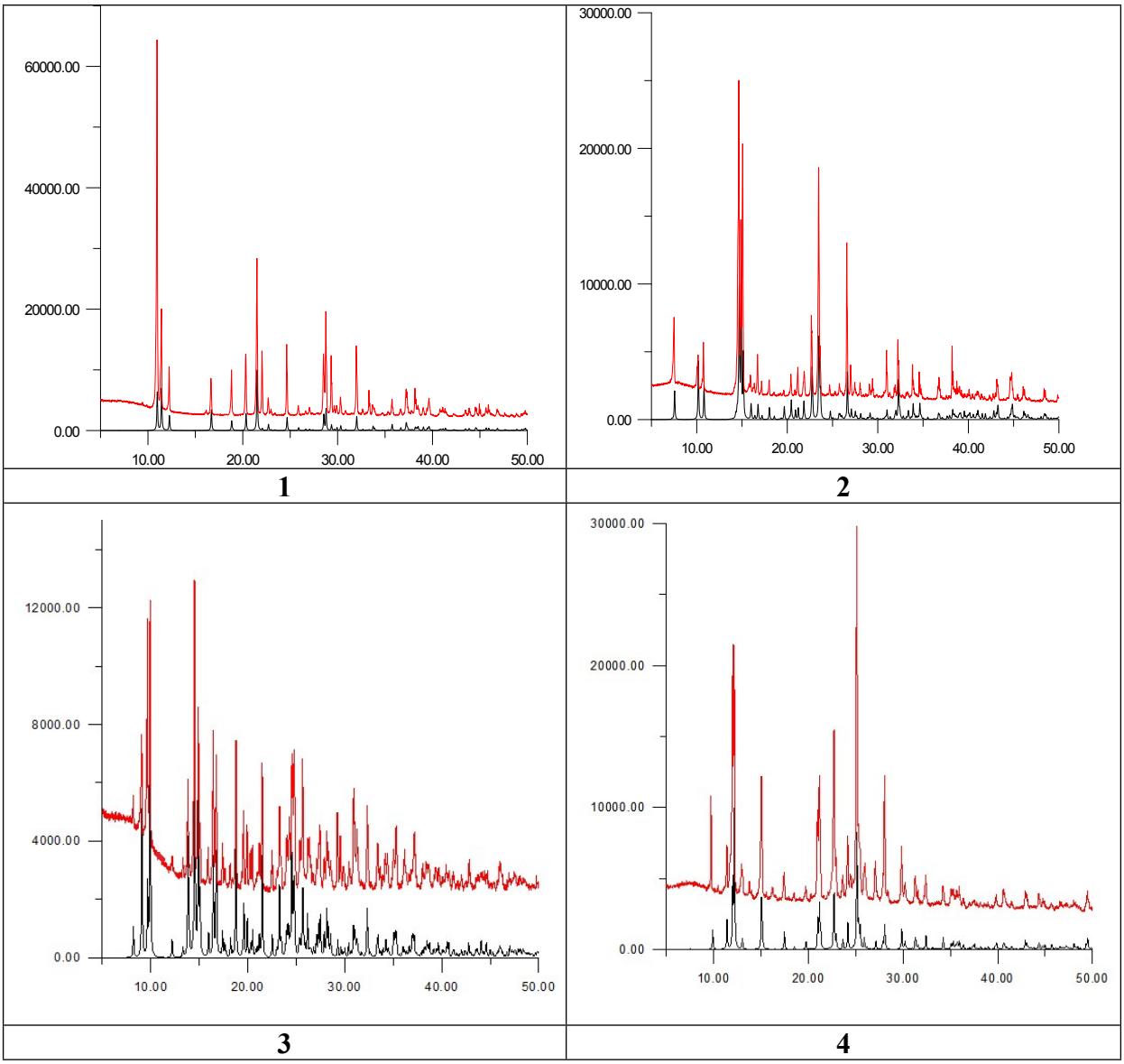


Figure S1. The powder XRD pattern of compounds **1–4** (experimental – red) and the simulation of the powder pattern from the crystal structure (black).

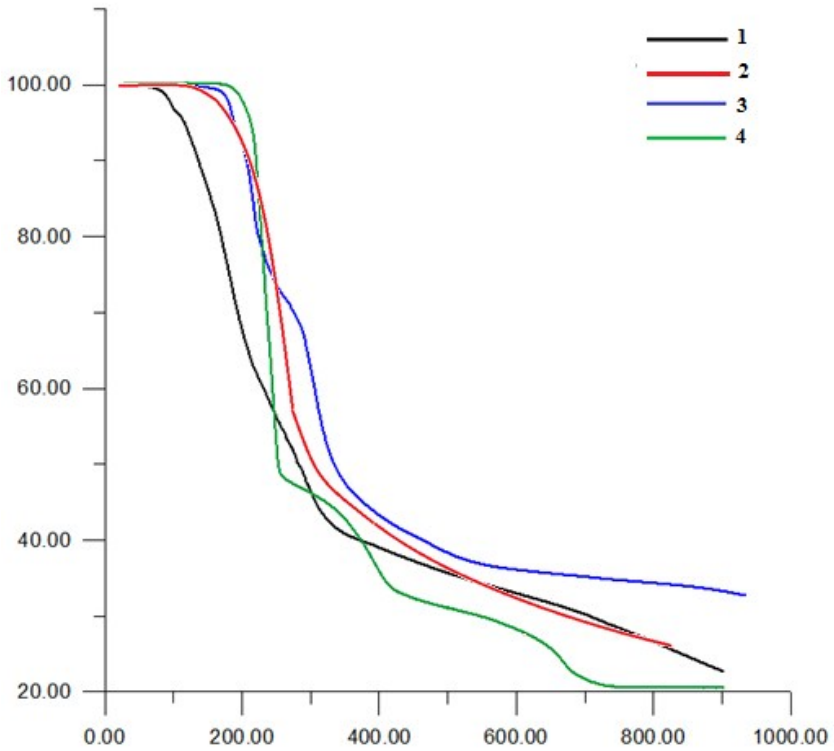


Figure S2. TG curves for complexes **1**, 2, **3** and **4.**

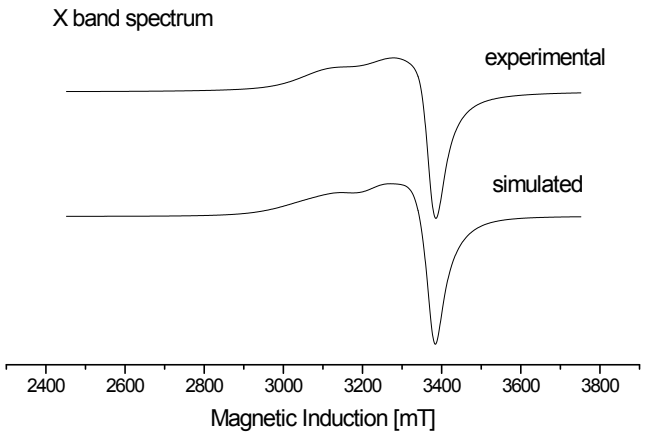


Figure S3. X band spectrum of the complex **1**; experimental and simulated spectrum
$g_x = 2.067$; $g_y = 2.102$, $g_z = 2.23$ $g_{av} = 2.14$

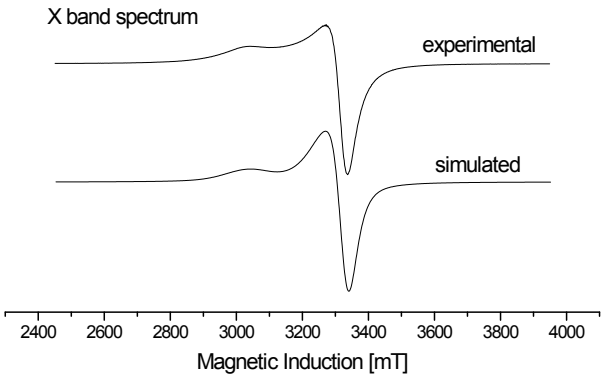


Figure S4. X band spectrum of the complex **2**; experimental and simulated spectrum $g_x = 2.067$; $g_y = 2.07$, $g_z = 2.25$ $g_{av} = 2.13$

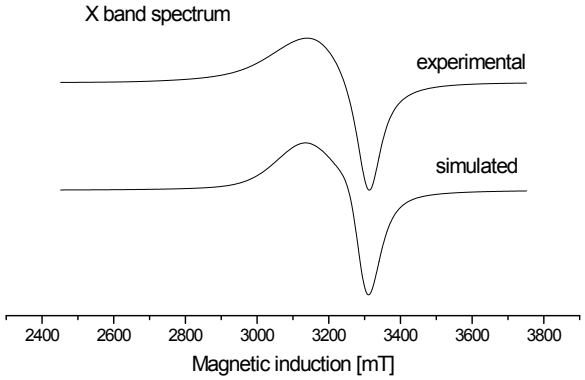


Figure S5. X band spectrum of the complex **3**; experimental and simulated spectrum $g_x = 2.081$; $g_y = 2.161$, $g_z = 2.161$ $g_{av} = 2.13$

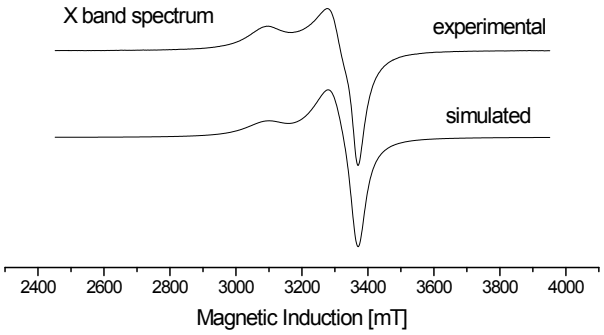


Figure S6. X band spectrum of the complex 4; experimental and simulated spectrum $g_x = 2.07$; $g_y = 2.107$, $g_z = 2.161$ $g_{av} = 2.12$

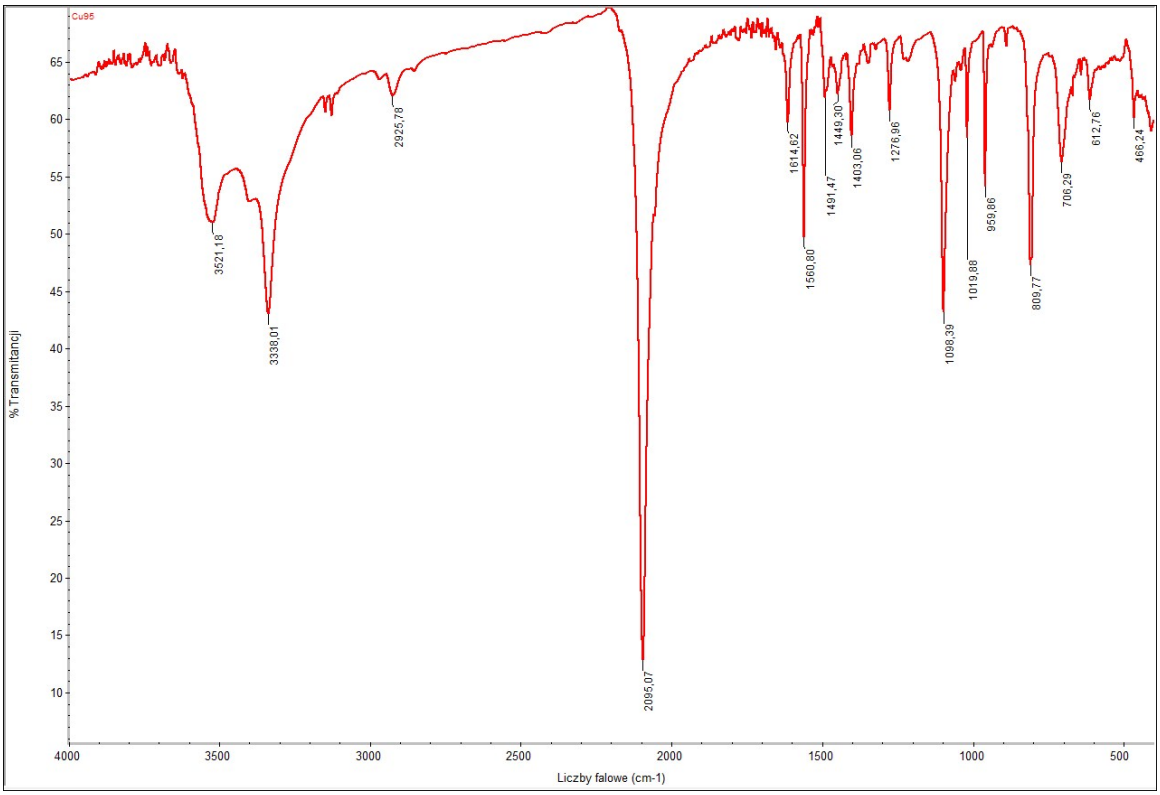


Figure S7. IR spectrum for **1**.

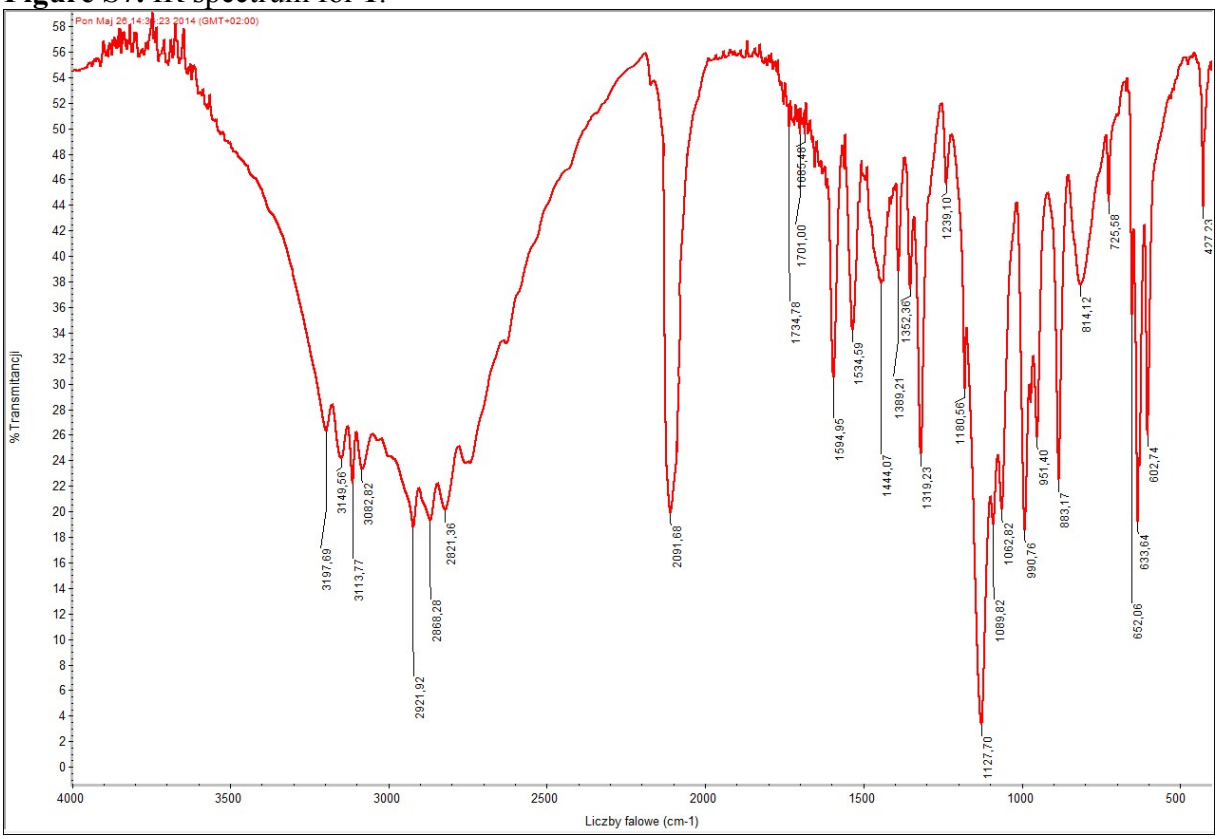


Figure S8. IR spectrum for **2**.

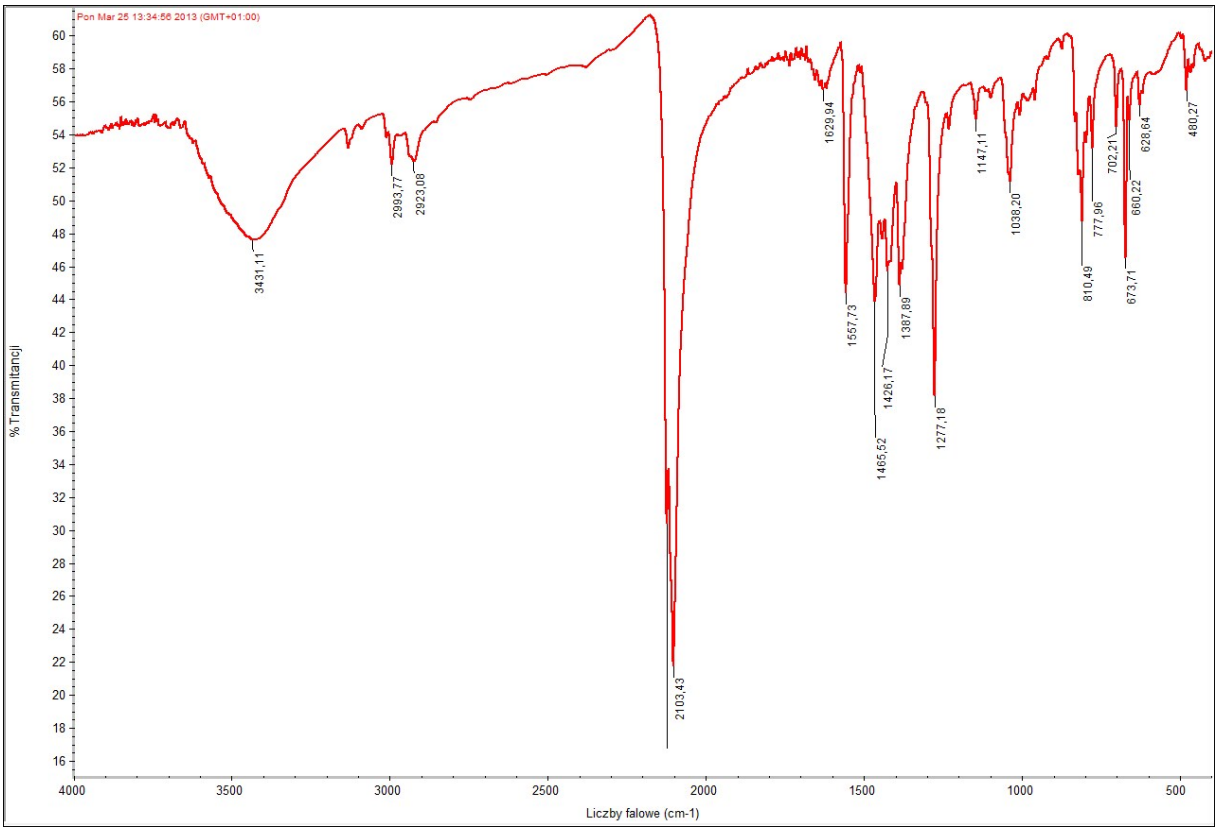


Figure S9. IR spectrum for **3**.

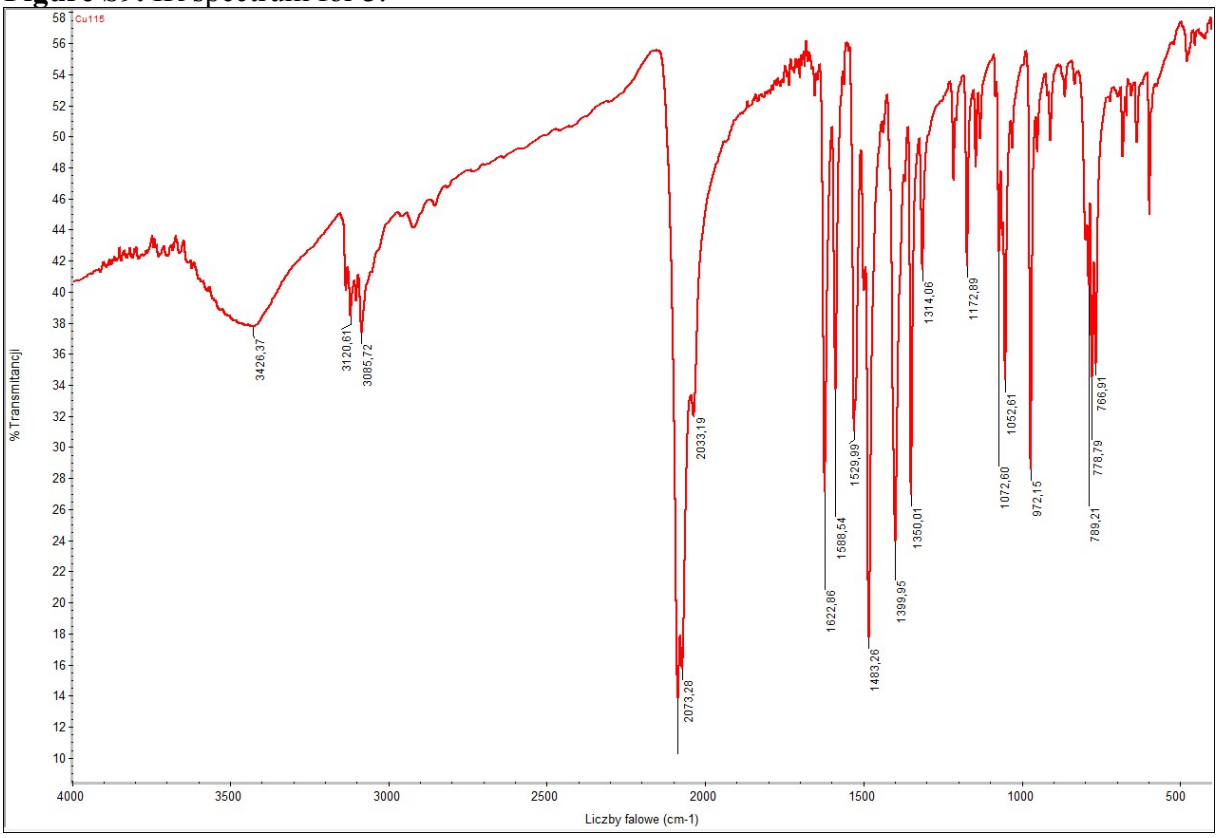


Figure S10. IR spectrum for **4**.