Electronic Supplementary Material (ESI) for RSC Advances.

The Supporting Information

Cobalt, nickel and copper complexes with glycinamide: structural insights and magnetic properties

Darko Vušak,[a] Neven Smrečki,[a] Biserka Prugovečki,[a] Ivica Đilović,[a] Inka Kirasić,[a] Dijana Žilić,[b] Senada Muratović,[b] and Dubravka Matković-Čalogović[*]*

[a]Division of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia E-mail: biserka@chem.pmf.hr

[b] Laboratory for Magnetic Resonances, Division of Physical Chemistry, Ruđer Bošković Institute, Bijenička 54, HR-10000 Zagreb, Croatia.

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[*]To whom correspondence should be addressed.

Tel: +385-1-4606347; +385-1-4606345. Fax: + 385-1-4606341.

E-mail: biserka@chem.pmf.hr

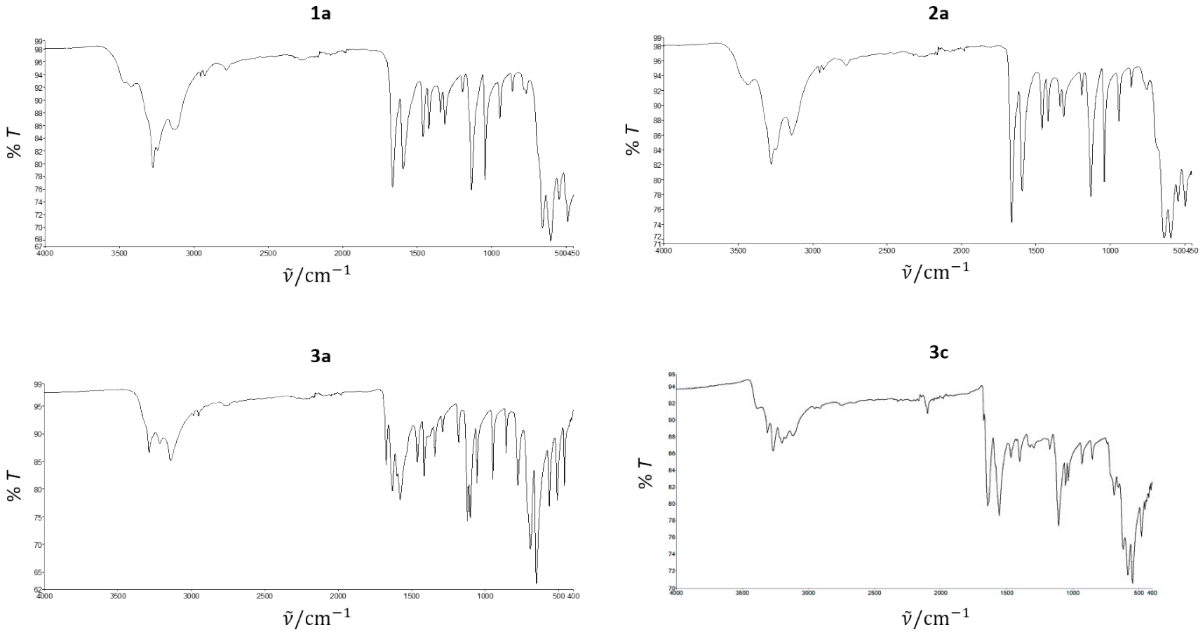


Fig. S1 Infrared spectra of cobalt ,nickel and copper mononuclear complexes **1**–**3a** and coordination polymer **3c**.

***β*-H_2LCl** **H_2LI**

Fig. S2 ORTEP drawing of ***β*-H_2LCl** and **H_2LI.** Displacement ellipsoids of non-hydrogen atoms are drawn at 50% probability level.

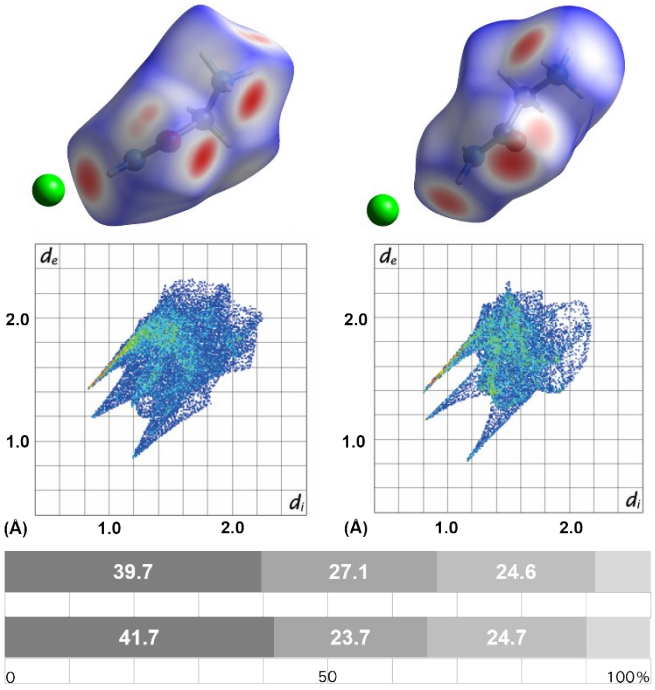
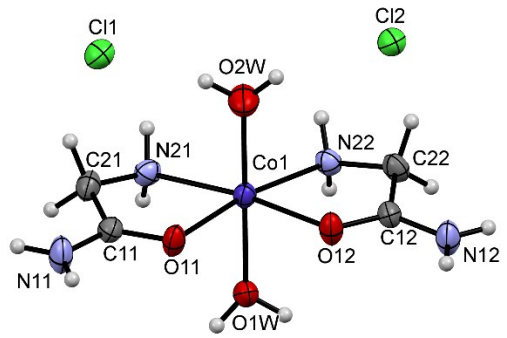
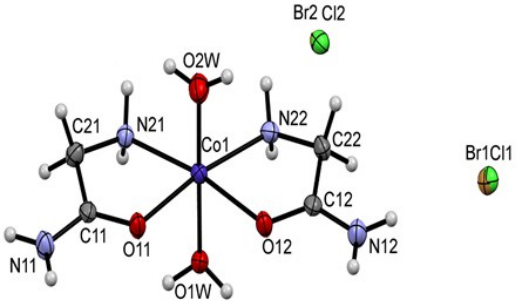


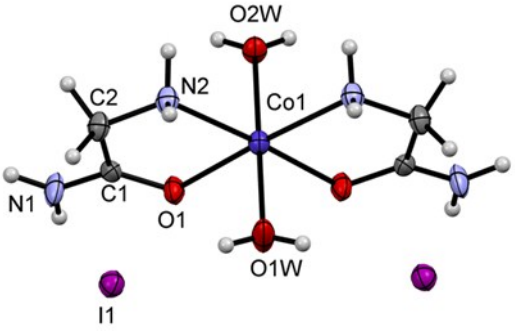
Fig. S3 Fingerprint plots for ***α*-H_2LCl** (left, CSD refcode: IHUTEM) and ***β*-H_2LCl** (right) were derived from Hirshfeld surfaces (top). Relative contributions (>5%) to the Hirshfeld surface for different type of intramolecular contacts in order: H···H; O···H; Cl···H and other contacts, (top ribbon – ***α*-H_2LCl**, bottom ribbon – ***β*-H_2LCl**).



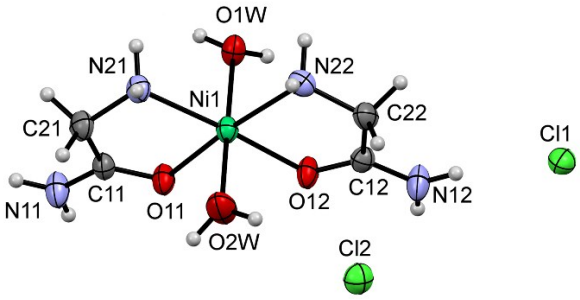
1a



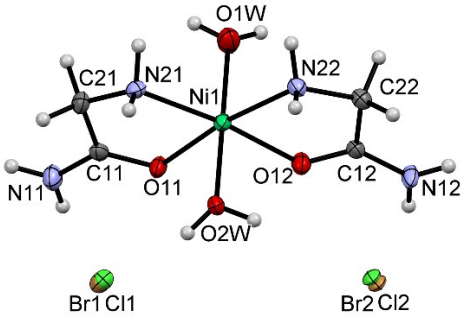
1b



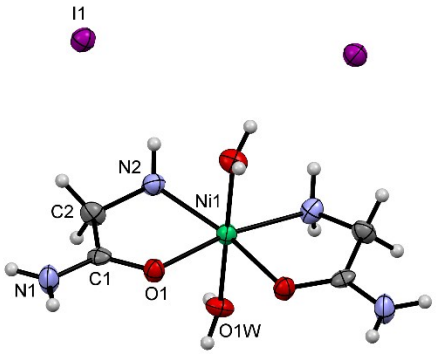
1c



2a



2b



2c$_{LT}$

Fig. S4 ORTEP drawing of **1a**, **1b**, **1c**, **2a**, **2b** and **2c$_{LT}$.** Displacement ellipsoids of non-hydrogen atoms are drawn at 50% probability level.

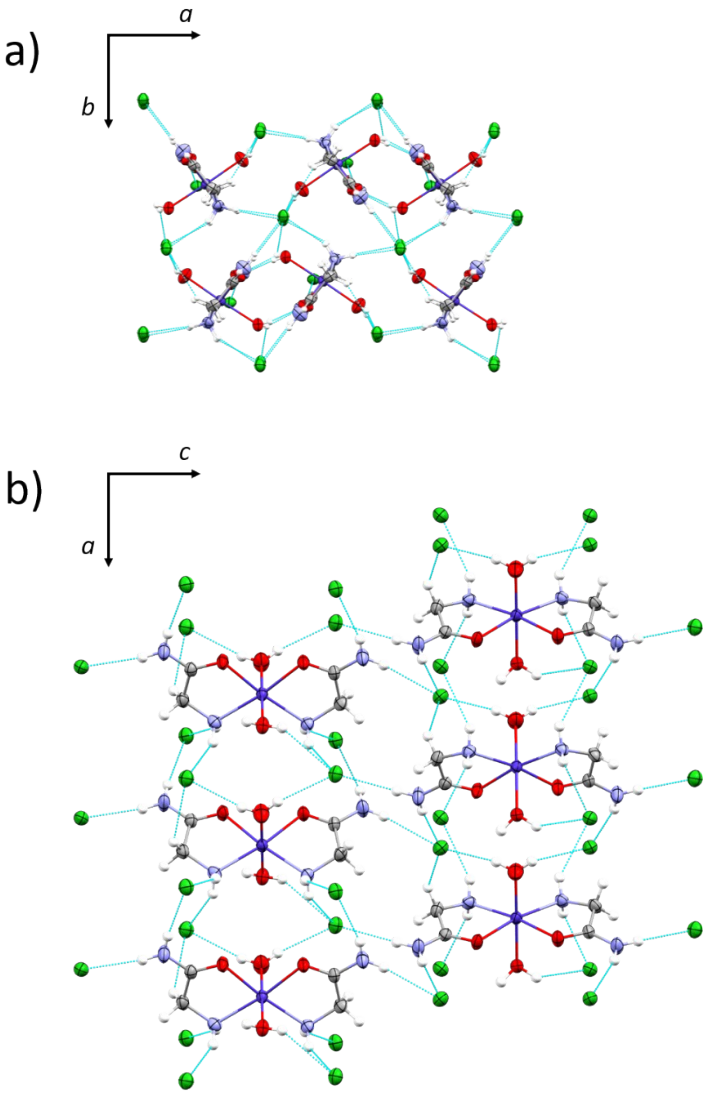


Fig. S5 a) Hydrogen bond network of **1a** in *a*-*b* plane; **b)**Hydrogen bonded chains of **1a** along *a* axis. Displacement ellipsoids of non-hydrogen atoms are drawn at 50% probability level.

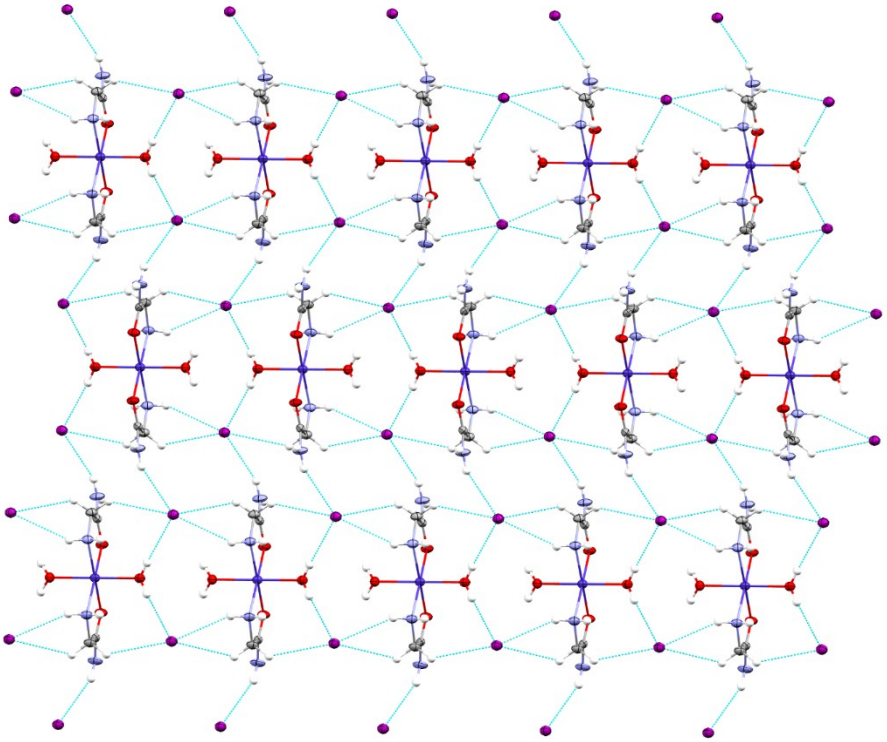


Fig. S6 Hydrogen bond network in **1c** parallel to *a*-*b* plane. Displacement ellipsoids of non-hydrogen atoms are drawn at 50% probability level.

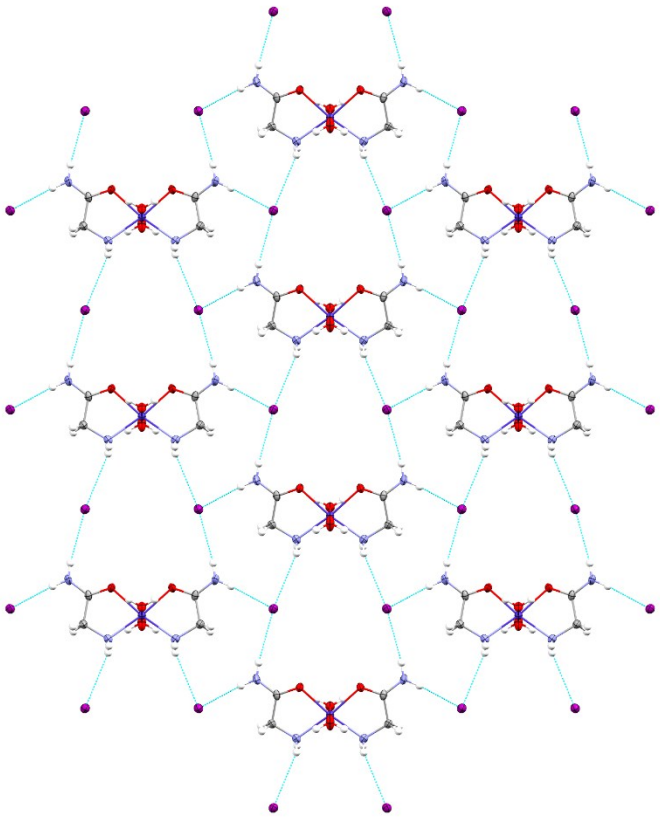


Fig. S7 Hydrogen bond network in **1c** parallel to *b*-*c* plane. Displacement ellipsoids of non-hydrogen atoms are drawn at 50% probability level.

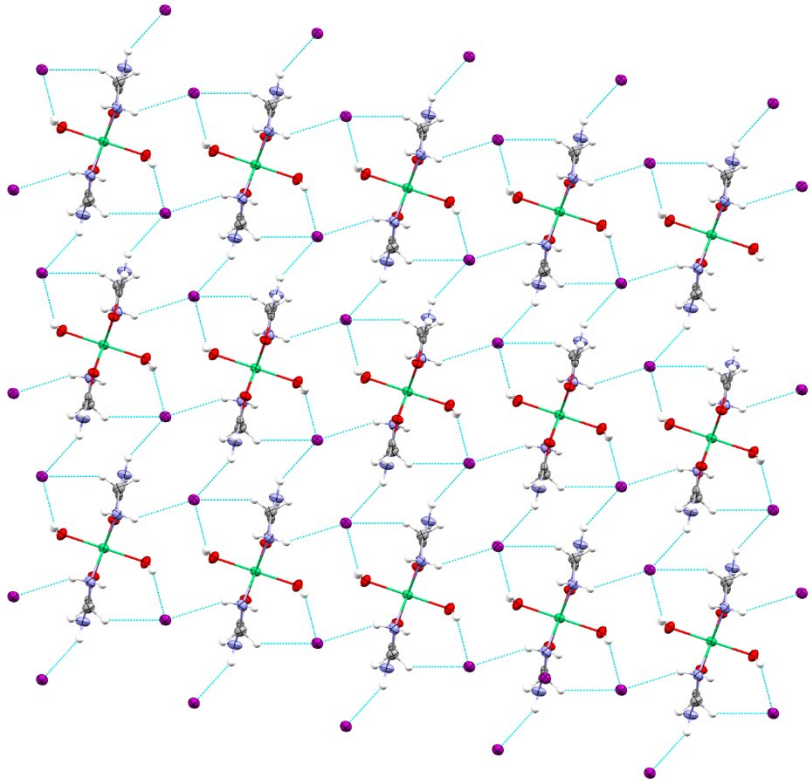


Fig. S8 Hydrogen bond network in **2c**$_{LT}$ parallel to *a*-*c* plane. Displacement ellipsoids of non-hydrogen atoms are drawn at 50% probability level.

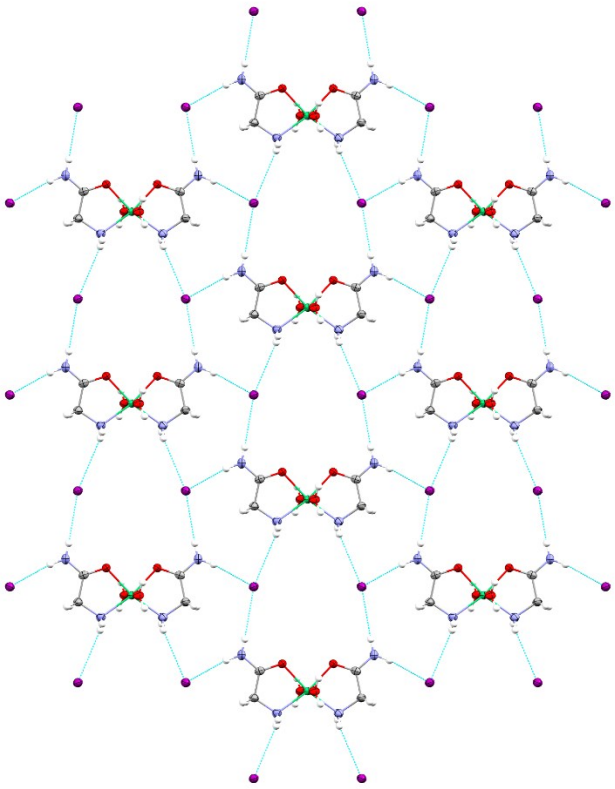


Fig. S9 Hydrogen bond network in **2c**$_{LT}$ parallel to *b*-*c* plane. Displacement ellipsoids of non-hydrogen atoms are drawn at 50% probability level.

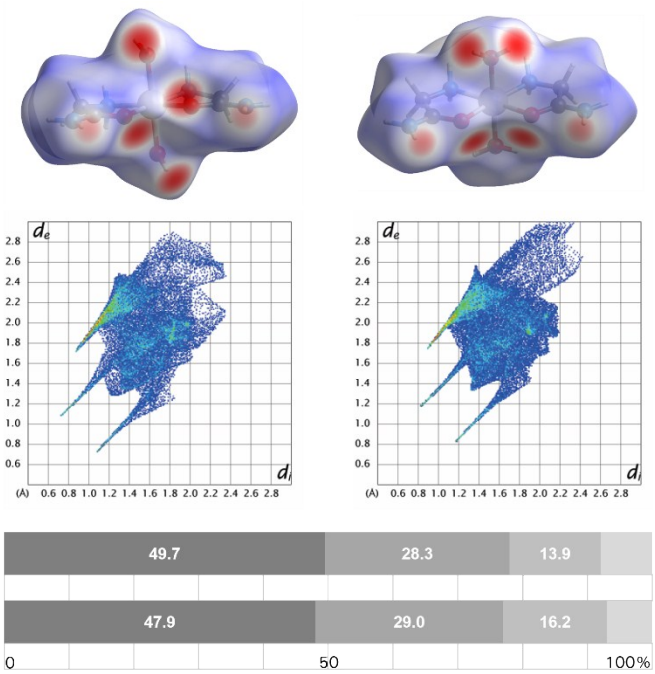


Fig. S10 Hirshfeld surfaces and fingerprint plots for the low temperature (left) and high temperature (right) polymorphs of compound **2c**. Relative contributions (> 5 %) to the Hirshfeld surface for different type of intramolecular contacts in order: H···H; H···I; O···H and other contacts (top ribbon – **2c$_{LT}$**, bottom ribbon – **2c$_{RT}$**).

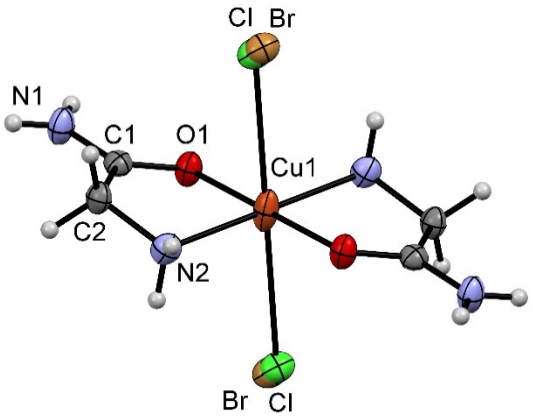


Fig. S11 ORTEP drawing of **3b.** Displacement ellipsoids of non-hydrogen atoms are drawn at 50% probability level.

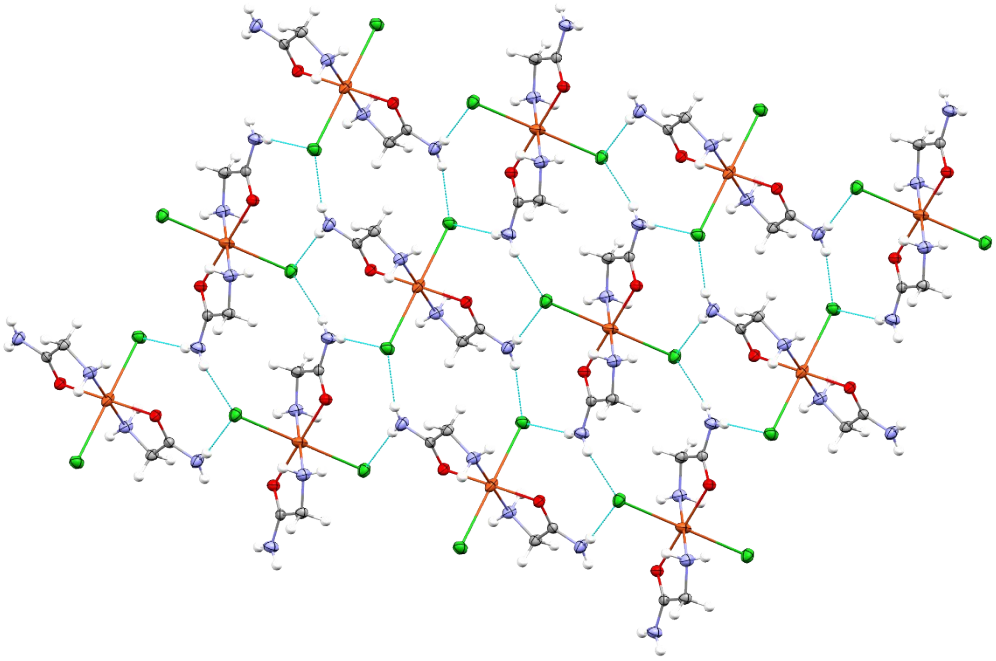


Fig. S12 Hydrogen bond network in **3a** along *b* axis. Displacement ellipsoids of non-hydrogen atoms are drawn at 50% probability level.

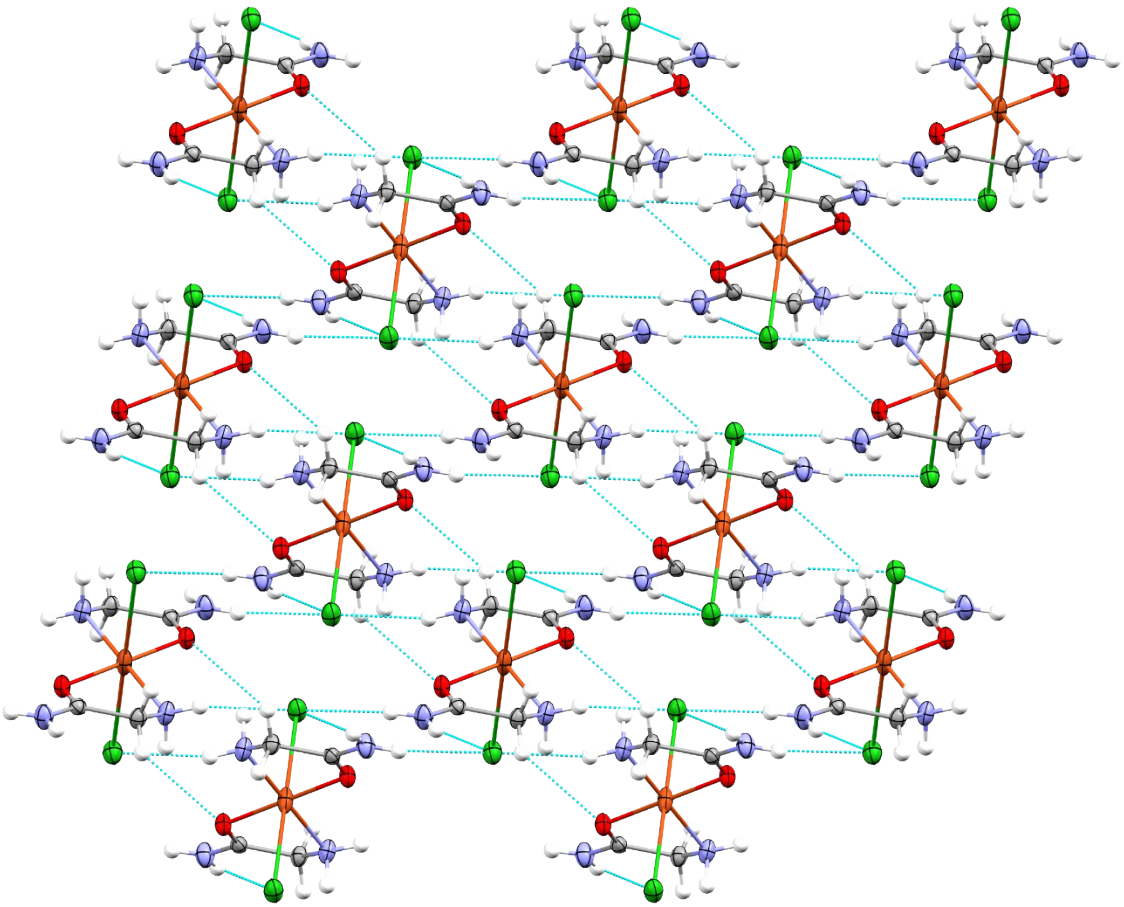


Fig. S13 Hydrogen bond network in **3a** parallel to *a*-*c* plane. Displacement ellipsoids of non-hydrogen atoms are drawn at 50% probability level.

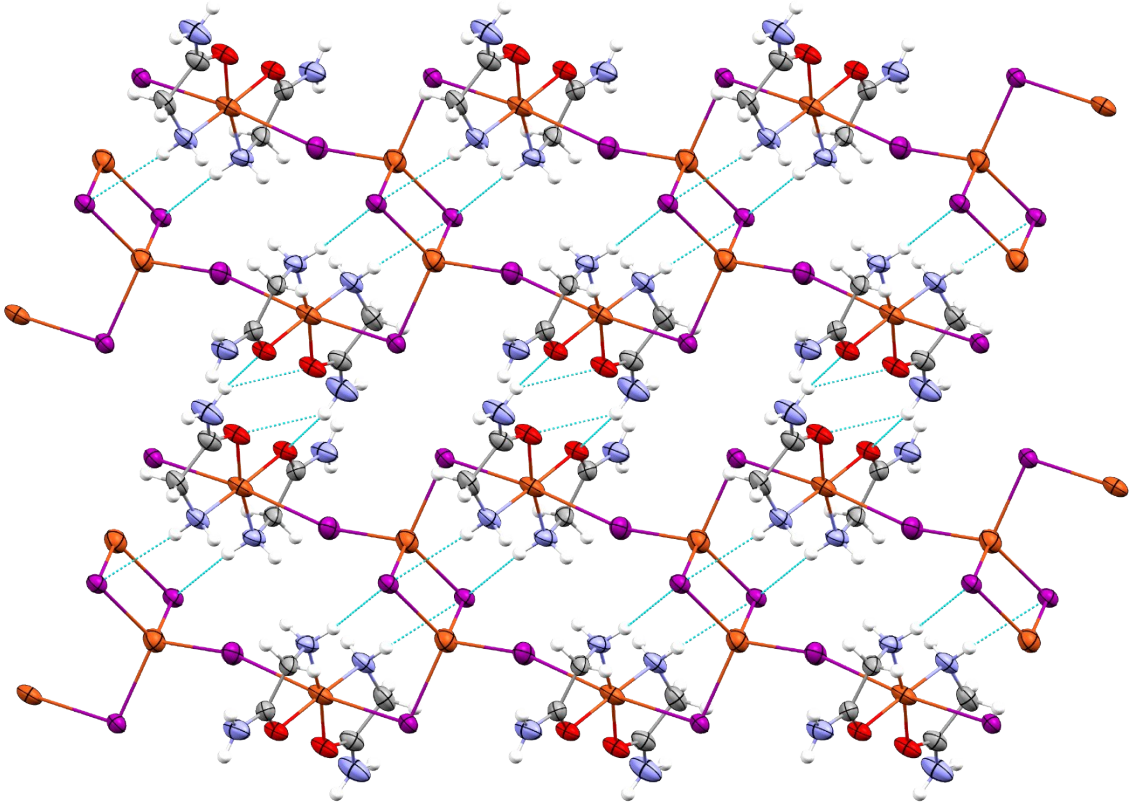


Fig. S14 Hydrogen bond network in **3c** parallel to *b-c* plane. Displacement ellipsoids of non-hydrogen atoms are drawn at 50% probability level.

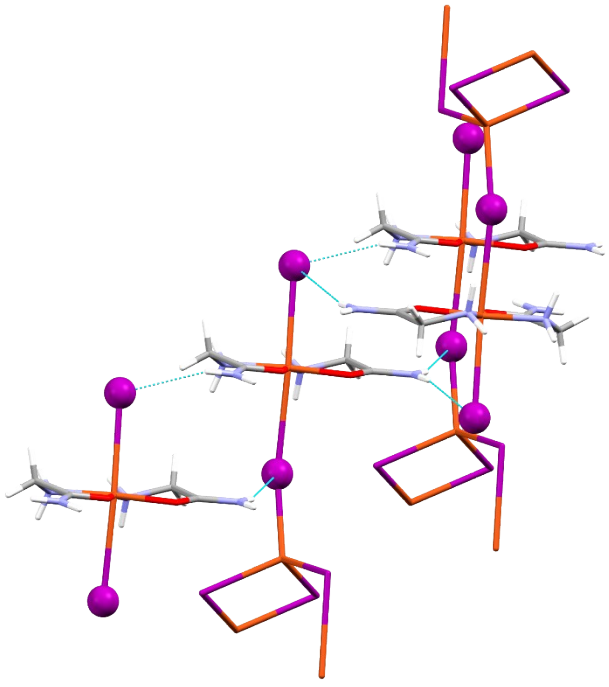


Fig. S15 Hydrogen bonding of axial iodide ions in **3c**.

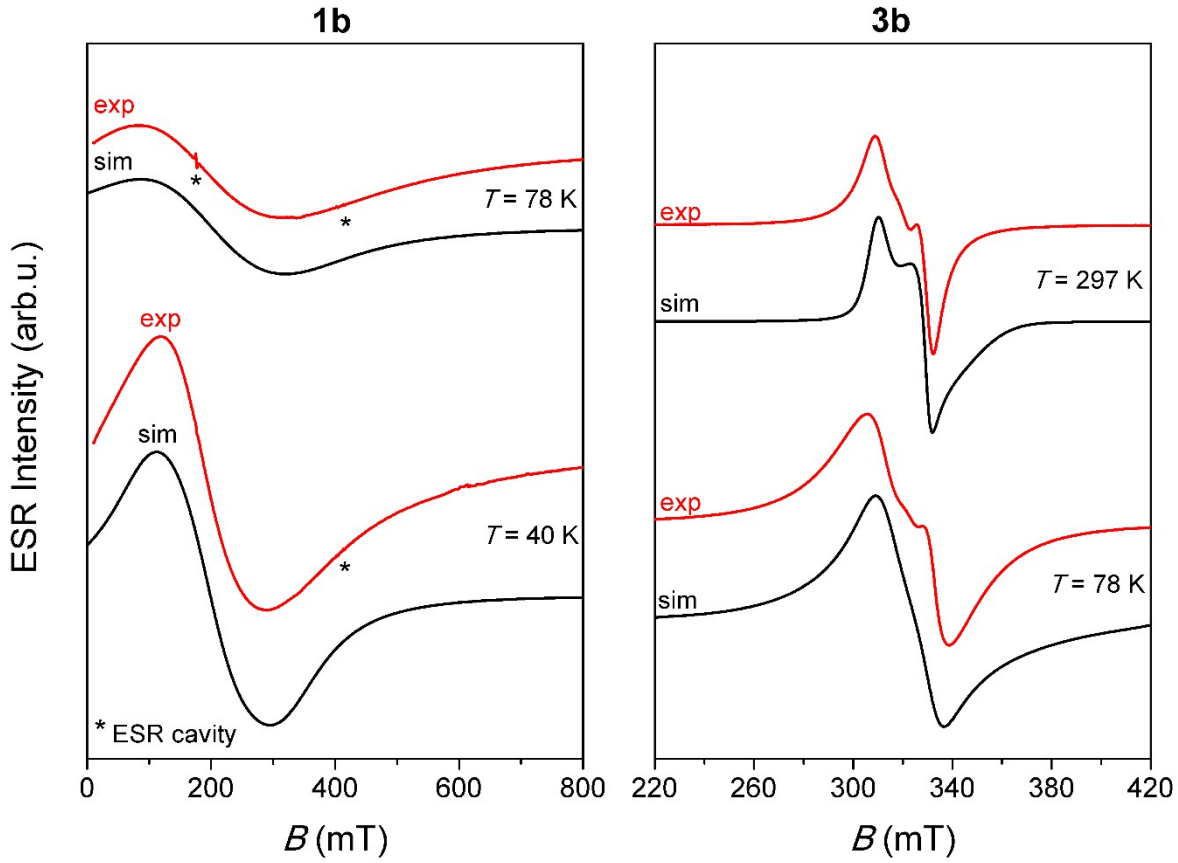


Fig. S16 Experimental (red lines) and simulated (black lines) ESR spectra of polycrystalline samples of the **1b** and **3b**. The ESR intensities of the spectra at different temperatures are presented in the real ratios. The narrow lines labeled with asterisks originate from the ESR cavity.

Table S1. Thermogravimetric analyses data

Compound	Water loss			Starting temperature of complex decomposition / °C
	T / °C	*w*(theor.) / %	*w*(exp.) / %	
1a	105 – 125	11.47	11.58	220
1b	110 – 130	9.97	10.31	230
1c[a]	/	/	/	/
2a	110 – 135	11.48	11.15	265
2b	105 – 135	10.13	10.03	260
2c$_{RT}$	100 – 160	7.25	7.35	255
3a	/	/	/	160
3b	/	/	/	165
3c	/	/	/	195

[a] Not measured due to small amount of sample

Table S2. Crystallographic data collection and structure refinement details for complexes **H_2LCl**, **H_2LI**, **1a**, **1b** and **1c**.

Compound	**β-H_2LCl**	**H_2LI**	**1a**	**1b**	**1c**
Empirical formula	$C_2H_7N_2O$, Cl	$C_2H_7N_2O$, I	$C_4H_{16}CoN_4O_4,Cl_2$	$C_4H_{16}CoN_4O_4$, $Br_{1.05}Cl_{0.95}$	$C_4H_{16}CoN_4O_4,I_2$
Formula weight	110.55	202.00	314.04	360.88	494.92
Crystal dimension/mm^3	0.11×0.21×0.77	0.07×0.10×0.16	0.12×0.29×0.36	0.25×0.40×0.50	0.07×0.10×0.16
Space group	$P2_1/m$	$Pca2_1$	$I4_1cd$	$I4_1cd$	$Pnma$
a/Å	4.6688(9)	18.6071(4)	11.3145(2)	11.3708(2)	7.3966(4)
b/Å	6.2057(13)	4.6876(1)	11.3145(2)	11.3708(2)	19.1784(8)
c/Å	8.898(2)	6.7360(2)	37.9735(8)	38.3225(14)	10.1512(4)
α/°	90	90	90	90	90
β/°	101.486(19)	90	90	90	90
γ/°	90	90	90	90	90
V/Å^3	252.64(9)	587.53(2)	4861.3(2)	4954.9(3)	1440.00(11)
D_{calc}/g cm^{-3}	252.64(9)	2.284	1.716	1.935	2.292
μ/mm^{-1}	0.615	5.330	1.853	4.989	5.482
F(000)	116	376	2576	2879	932
ϑ range/°	4.6–30.0	4.3–32.7	4.2–27.0	4.3–27.0	4.3–27.0
T/K	293	293	293	150	150
Radiation wavelength	0.71073	0.71073	0.71073	0.71073	0.71073
Diffractometer type					
Range of h, k, l	–6–6; –7–8; –12–12	–28–27; –7–6; –9–10	–14–14; –14–14; –48–48	–12–14; –12–14; –48–40	–5–9; –23–24; –12–12
Reflections collected	1665	5280	26763	15188	4648
Independent reflections	795	1895	2660	2501	1606
Observed reflections ($I \geq 2\sigma$)	619	1665	2592	2324	1211
Absorption correction					
R_{int}	0.027	0.023	0.024	0.036	0.042
R^a, $wR^b[I \geq 2\sigma(I)]$	0.0406, 0.1004	0.0256, 0.0488	0.0169, 0.0426	0.0238, 0.0538	0.0327, 0.0602
Goodness-of-fit, S^c	1.12	1.11	1.13	1.03	1.03
H atom treatment	difference map	difference map	mixed	mixed	mixed
No. of parameters	55	64	153	161	81
No. of restraints	0	0	0	0	0
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	–0.34, 0.42	–0.43, 0.67	–0.17, 0.16	–0.27, 0.31	–0.65, 0.94

[a] $R = \Sigma \left|\left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$; [b] $wR = [\Sigma(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$; [c] $S = \Sigma[w(F_o^2 - F_c^2)^2 / (N_{obs} - N_{param})]^{1/2}$

Table S3. Selected distances ([Å]) and angles ([°]) in the crystal structures of **α-H_2LCl** [ref IHUTEM], **β-H_2LCl** and **H_2LI**

Bond lengths [Å]

	α-H_2LCl [ref IHUTEM]	**β-H_2LCl**	**H_2LI**
O1–C1	1.2275(18)	1.228(3)	1.220(5)
N1–C1	1.315(2)	1.318(4)	1.335(6)
N2–C2	1.462(2)	1.477(4)	1.472(5)
C1–C2	1.516(2)	1.511(4)	1.514(5)

Bond angles [°]

	α-H_2LCl [ref IHUTEM]	**β-H_2LCl**	**H_2LI**
O1–C1–N1	124.49(14)	124.6(2)	124.6(4)
O1–C1–C2	120.25(13)	119.7(2)	119.0(4)
N1–C1–C2	115.25(13)	115.8(2)	115.2(4)
N2–C2–C1	110.57(13)	110.4(2)	110.2(3)

Torsion angles [°]

	α-H_2LCl [ref IHUTEM]	**β-H_2LCl**	**H_2LI**
O1–C1–C2–N2	-31.80(18)	0.00(2)	-2(2)
N1–C1–C2–N2	149.64(15)	180.00(2)	-169.6(18)

Table S4. Geometry of selected intermolecular hydrogen bonds ([Å],[°]) for compounds **β-H_2LCl** and **H_2LI**

	D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	D–H···A [°]
β-H_2LCl	N1–H1A···O1[a]	0.83(3)	2.15(3)	2.913(3)	154(2)
	N1–H1B···Cl1[b]	0.87(3)	2.48(3)	3.343(3)	179(3)
	N2–H2B···Cl1[c]	0.91(4)	2.29(4)	3.172(3)	166(3)
	N2–H2C···Cl1[d]	0.90(2)	2.40(2)	3.2132(10)	150.6(18)
H_2LI	N1–H1A···O1[e]	0.84(6)	2.19(5)	2.935(5)	149(4)
	N1–H1B···I1[f]	0.88(5)	2.95(4)	3.796(3)	162(8)
	N2–H2C···I1[g]	0.89	2.73	3.619(19)	178
	N2–H2D···I1	0.89	2.73	3.577(3)	160
	N2–H2E···I1[h]	0.89	2.90	3.648(19)	144
	C2–H2B···O1[d]	0.97	2.59	3.009(5)	107

[a] 1+x,y,z; [b] -1+x,y,z; [c]x,y,1+z,-1/2+y,2-z; [d] 1-x,-1/2+y,[e] 1-z; [f]-1/2+x,-y,z; [g] -1-x,-y,1/2+z; [h] -1-x,-y,-1/2+z

Table S5. Crystallographic data collection and structure refinement details for complexes **2a**, **2b, 2c, 3a, 3b** and **3c**.

Compound	**2a**	**2b**	**2c$_{LT}$**	**2c$_{RT}$**	**3a**	**3b**	**3c**
Empirical formula	$C_4H_{16}N_4NiO_4,Cl_2$	$C_4H_{16}N_4NiO_4$, $Br_{0.94}Cl_{1.06}$	$C_4H_{16}N_4NiO_4,I_2$	$C_4H_{16}N_4NiO_4,I_2$	$C_4H_{12}Cl_2Cu_1N_4O_2$	$C_4H_{12}Br_{1.30}Cl_{0.70}CuN_4O_2$	$C_4H_{12}Cu_2I_3N_4O_2$
Formula weight	313.82	355.61	496.72	496.72	282.63	340.41	655.96
Crystal dimension/mm^3	0.14x0.40x0.60	0.33×0.45×0.54	0.14×0.21×0.42	0.19×0.22×0.28	0.40×0.40×0.45	0.19×0.52×0.58	0.04×0.14×0.35
Space group	*I* 4$_1$*cd*	*I* 4$_1$*cd*	*I* 2/*a*	P *nma*	*P* 2$_1$/*n*	*P* 2$_1$/*n*	$P\bar{1}$
a/Å	11.2394(5)	11.3175(3)	7.2589(7)	7.5456(3)	6.8813(2)	7.0098(5)	8.0185(4)
b/Å	11.2394(5)	11.3175(3)	10.3706(10)	18.9706(7)	7.7420(2)	7.8128(3)	8.6901(4)
c/Å	37.594(4)	38.0842(14)	19.2258(17)	10.1902(3)	9.2635(2)	9.4100(5)	11.0929(5)
α/°	90	90	90	90	90	90	84.575(4)
β/°	90	90	98.742(9)	90	101.779(3)	101.963(6)	77.367(4)
γ/°	90	90	90	90	90	90	72.679(4)
V/Å^3	4749.0(7)	4878.1(3)	1430.5(2)	1458.67(9)	483.12(2)	504.16(5)	719.69(6)
D_{calc}/g cm^{-3}	1.756	1.936	2.306	2.262	1.943	2.242	3.027
μ/mm^{-1}	2.086	4.905	5.675	5.565	2.787	7.478	9.378
F(000)	2592	2862	936	936	286	333	594
ϑ range/°	4.4–33.0	4.3–27.0	4.3–27.0	4.3–27.0	4.3–28.0	4.4–27.0	4.2–27.0
T/K	150	150	150	295	293	293	293
Radiation wavelength	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Diffractometer type							
Range of *h*, *k*, *l*	–15–15; –17–16; –55–56	–14–11; –14–11; –48–48	–9–9; –13–13; –21–24	–9–9; –20–24; –13–7	-9–9; -10–10; –12–12	–8–8; –9–9; –12–12	–10–10; –11–11; –14–14
Reflections collected	21338	12846	2506	5770	11873	4025	7861
Independent reflections	4042	3236	2506	1626	1159	1092	3084
Observed reflections ($I \geq 2\sigma$)	3480	2950	2208	1374	1139	985	2548
Absorption correction							
R_{int}	0.030	0.031	0.038	0.024	0.016	0.028	0.039
R^a, $wR^b[I \geq 2\sigma(I)]$	0.0269, 0.0592	0.0246, 0.0498	0.0353, 0.1020	0.0299, 0.0698	0.0151, 0.0479	0.0238, 0.0571	0.0259, 0.0686
Goodness-of-fit, S^c	1.08	1.09	1.19	1.09	0.98	1.12	0.84
H atom treatment	mixed	mixed	mixed	mixed	difference map	calculated	calculated
No. of parameters	149	167	78	81	86	65	137
No. of restraints	0	0	0	0	0	0	0
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	–0.29, 0.43	–0.29, 0.34	–0.75, 2.28	–0.77, 0.92	–0.24, 0.42	–0.50, 0.29	–1.15, 1.08

[a] $R = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$; [b] $wR = [\Sigma(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$; [c] $S = \Sigma[w(F_o^2 - F_c^2)^2 / (N_{obs} - N_{param})]^{1/2}$

Table S6. Distances ([Å]) and angles ([°]) within the polyhedra of cobalt coordination spheres in the crystal structures of **1a**, **1b** and **1c**.

Bond lengths [Å]

	1a	**1b**	**1c**
Co1–O1w	2.1445(14)	2.132(3)	2.078(6)
Co1–O2w	2.0988(18)	2.089(3)	2.109(5)
Co1–O1 / Co1–O^{i}			2.112(3)
Co1–O11	2.103(2)	2.096(4)	
Co1–O12	2.097(2)	2.091(4)	
Co1–N2 / Co1–N2^{i}			2.122(4)
Co1–N21	2.128(3)	2.116(4)	
Co1–N22	2.125(3)	2.121(4)	
Bond angles [°]			
O1w–Co1–O2w	178.26(6)	178.73(13)	178.6(2)
O1w–Co1–O1 / O1w–Co1–O1^{i}			89.35(14)
O1w–Co1–O11	87.84(7)	89.59(15)	
O1w–Co1–O12	89.51(8)	87.74(14)	
O1w–Co1–N2 / O1w–Co1–N2^{i}			93.07(14)
O1w–Co1–N21	88.02(8)	88.18(15)	
O1w–Co1–N22	87.88(8)	87.97(16)	
O2w–Co1–O1 / O2w–Co1–O1^{i}			89.70(13)
O2w–Co1–O11	90.75(8)	89.82(15)	
O2w–Co1–O12	87.84(7)	91.16(15)	
O2w–Co1–N2 / O2w–Co1–N2^{i}			87.76(13)
O2w–Co1–N21	92.72(8)	92.82(16)	
O2w–Co1–N22	93.36(8)	92.45(16)	
O1–Co1–O1^{i}			94.32(13)
O11–Co1–O12	91.67(8)	92.09(13)	
O1–Co1–N2 / O1^{i}–Co1–N2^{i}			78.89(14)
O11–Co1–N21	79.20(10)	79.68(15)	
O12–Co1–N22	79.72(10)	79.39(15)	
O1–Co1–N2^{i} / O1^{i}–Co1–N2			172.75(14)
O11–Co1–N22	170.41(10)	171.22(15)	
O12–Co1–N21	170.62(10)	170.84(15)	
N2–Co1–N2^{i}			107.77(16)
N21–Co1–N22	109.22(9)	108.66(16)	

^{i} x,1/2-y,z

Table S7. Distances ([Å]) and angles ([°]) within the polyhedra of nickel coordination spheres in the crystal structures of **2a**, **2b** and **2c$_{RT}$**.

Bond lengths [Å]

	2a	**2b**	**2c$_{RT}$**
Ni1–O1w	2.1120(17)	2.081(3)	2.094(5)
Ni1–O2w	2.083(2)	2.110(2)	2.078(6)
Ni1–O1 / Ni1–O^{i}			2.046(3)
Ni1–O11	2.039(2)	2.039(4)	
Ni1–O12	2.040(2)	2.050(4)	
Ni1–N2 / Ni1–N2^{i}			2.072(4)
Ni1–N21	2.067(3)	2.068(4)	
Ni1–N22	2.069(3)	2.077(4)	
Bond angles [°]			
O1w–Ni1–O2w	179.60(10)	179.80(14)	176.0(3)
O1w–Ni1–O1 / O1w–Ni1–O1^{i}			89.57(15)
O1w–Ni1–O11	90.05(9)	91.50(15)	
O1w–Ni1–O12	88.52(9)	90.10(15)	
O1w–Ni1–N2 / O1w–Ni1–N2^{i}			89.01(15)
O1w–Ni1–N21	88.31(9)	91.80(15)	
O1w–Ni1–N22	88.02(9)	91.63(15)	
O2w–Ni1–O1 / O2w–Ni1–O1^{i}			87.66(19)
O2w–Ni1–O11	90.00(10)	88.49(14)	
O2w–Ni1–O12	91.09(10)	90.10(14)	
O2w–Ni1–N2 / O2w–Ni1–N2^{i}			93.37(19)
O2w–Ni1–N21	92.10(10)	88.00(14)	
O2w–Ni1–N22	91.88(11)	88.41(14)	
O1–Ni1–O1^{i}			91.56(12)
O11–Ni1–O12	90.97(11)	91.43(14)	
O1–Ni1–N2 / O1^{i}–Ni1–N2^{i}			81.21(13)
O11–Ni1–N21	81.56(13)	81.39(15)	
O12–Ni1–N22	81.30(13)	81.38(15)	
O1–Ni1–N2^{i} / O1^{i}–Ni1–N2			172.64(13)
O11–Ni1–N22	172.05(10)	172.16(15)	
O12–Ni1–N21	171.90(10)	172.62(15)	
N2–Ni1–N2^{i}			105.99(14)
N21–Ni1–N22	106.04(9)	105.69(14)	

^{i} x,1/2-y,z

Table S8. Geometry of selected intra- and intermolecular hydrogen bonds ([Å],[°]) for compounds **1a, 1b** and **1c.**

	D−H···A	D−H [Å]	H···A [Å]	D···A [Å]	D−H···A [°]
1a	O1W−H1WA···Cl2[a]	0.850(4)	2.659(13)	3.279(2)	130.9(12)
	O1W−H1WA···O12[a]	0.850(4)	2.332(10)	2.966(3)	131.8(12)
	O1W−H1WB···O11[a]	0.850(5)	2.029(8)	2.844(3)	160.3(11)
	O2W−H2WA···Cl2[b]	0.850(6)	2.455(5)	3.272(2)	161.8(6)
	O2W−H2WB···Cl1[b]	0.850(6)	2.394(6)	3.217(2)	163.4(9)
	N11−H11A···Cl1	0.86	2.41	3.262(3)	173
	N11−H11B···Cl2[c]	0.86	2.40	3.252(3)	174
	N12−H12A···Cl2	0.86	2.54	3.376(3)	166
	N12−H12B···Cl1[d]	0.86	2.47	3.320(3)	170
	N21−H21C···Cl1[a]	0.89	2.63	3.423(2)	149
	N21−H21D···Cl1[e]	0.89	2.58	3.396(2)	152
	N12−H12B···Cl1[a]	0.89	2.60	3.355(2)	144
	N12−H12B···Cl1[e]	0.89	2.53	3.315(2)	148
1b	O2W−H2WA···Br2	0.84(4)	2.44(4)	3.269(8)	168(4)
	O2W−H2WB···Br1[f]	0.85(6)	2.52(5)	3.301(9)	154(6)
	O2W−H2Wb···Cl1[f]	0.85(6)	2.49(6)	3.27(2)	154(6)
	O1W−H1WA···O12[g]	0.85(4)	2.04(5)	2.835(5)	157(5)
	O1W−H1WB···Br1[h]	0.84(3)	2.76(5)	3.370(9)	130(5)
	O1W−H1WB···O11[g]	0.84(3)	2.31(6)	2.934(5)	131(5)
	N11−H11A···Br1[i]	0.88	2.55	3.413(8)	166
	N11−H11A···Cl1[i]	0.88	2.55	3.409(19)	165
	N11−H11B···Br2[j]	0.88	2.50	3.372(9)	170
	N11−H11B···Cl2[j]	0.88	2.49	3.36(2)	170
	N12−H12A···Br2[k]	0.88	2.46	3.340(8)	173
	N12−H12B···Br1	0.88	2.40	3.274(9)	172
	N21−H21C···Br1[h]	0.91	2.60	3.389(8)	146
	N21−H21C···Cl1[h]	0.91	2.56	3.354(18)	146
	N21−H21D···Br1[l]	0.91	2.57	3.373(8)	147
	N21−H21D···Cl1[l]	0.91	2.55	3.363(18)	148
	N22−H22C···Br2[m]	0.91	2.63	3.440(8)	149

	N22−H22C···Cl2[m]	0.91	2.61	3.42(2)	148
	N22−H22D···Cl2[n]	0.91	2.64	3.462(8)	150
	N22−H22B···Br2[n]	0.91	2.65	3.47(2)	150
	N1−H1A···I1[o]	0.88	2.86	3.703(4)	161
	N1−H1B···I1[p]	0.88	2.85	3.688(4)	159
1c	O1W−H1W···I1	0.85(4)	2.66(4)	3.507(3)	177(5)
	N2−H2D···I1[r]	0.91	2.94	3.733(4)	147
	O2W−H2W···O1[o]	0.85(4)	2.00(5)	2.789(5)	154(4)

[a] 1-x,-y,z; [b] -1/2+x,-1/2-y,z; [c]x,y,1+z,-1/2+y,2-z; [d] -y,-1/2+x,1/4+z,[e] 1/2-x,-1/2+y,z; [f]1+y,3/2-x,1/4+z; [g]2-x,-y,z ; [h] 1/2+y,-1+x,1/4+z; [i]3/2-y,1-x,1/4+z ; [j]1/2+y,-1+x,1/4+z ; [k] 5/2-x,-1/2+y,z; [l] 1-y,-1/2+x,1/4+z; [m]-1/2+x,1/2-y,z ; [n]2-x,1-y,z ;[o]1/2+x,y,1/2-z; [p]1-x,1-y,1-z; [r]1+x,y,z

Table S9. Geometry of selected intra- and intermolecular hydrogen bonds ([Å],[°]) for compounds **2a, 2b** and **2c$_{LT}$.**

	D−H···A	D−H [Å]	H···A [Å]	D···A [Å]	D−H···A [°]
2a	O1W−H1WB···Cl1[a]	0.83(3)	2.53(3)	3.244(3)	144(3)
	O1W−H1WB···O11[b]	0.84(3)	2.46(3)	2.957(3)	119(3)
	O2W−H2WB···Cl1[c]	0.83(3)	2.47(3)	3.271(3)	161(3)
	O1W−H1WA···O12[b]	0.85(3)	2.03(3)	2.845(3)	161(3)
	O2W−H2WA···Cl2	0.84(2)	2.43(2)	3.216(3)	156(3)
	N11−H11A···Cl1[d]	0.86	2.52	3.357(3)	166
	N11−H11B···Cl2[a]	0.86	2.44	3.290(3)	171
	N12−H12A···Cl2[e]	0.86	2.39	3.248(3)	174
	N12−H12B···Cl1	0.86	2.37	3.230(3)	173
	N21−H21C···Cl1[a]	0.89	2.61	3.355(2)	142
	N21−H21D···Cl1[f]	0.89	2.54	3.305(2)	145
	N22−H22C···Cl2[g]	0.89	2.63	3.412(2)	147
	N22−H22D···Cl2[b]	0.89	2.59	3.384(2)	149
2b	O1W−H1WB···Br1[h]	0.84(5)	2.50(5)	3.301(16)	162(5)
	O1W−H1WB···Cl1[h]	0.84(5)	2.47(6)	3.28(4)	162(5)
	O2W−H2WA···Br2[i]	0.84(4)	2.74(5)	3.367(12)	132(6)
	O2W−H2WA···Cl2[i]	0.84(4)	2.56(5)	3.205(19)	134(6)
	O2W−H2WA···O12[i]	0.84(4)	2.37(6)	2.931(4)	125(4)
	O2W−H2WB···O11[i]	0.83(5)	2.06(6)	2.835(4)	157(5)
	O1W−H1WA···Br2[h]	0.81(4)	2.50(4)	3.284(12)	164(4)
	O1W−H1WA···Cl2[h]	0.81(4)	2.50(5)	3.299(19)	168(5)
	N11−H11A···Br1	0.88	2.45	3.327(15)	175
	N11−H11A···Cl1	0.88	2.41	3.28(4)	173
	N11−H11B···Br2[j]	0.88	2.36	3.232(12)	171
	N11−H11B···Cl2[j]	0.88	2.51	3.385(19)	173
	N12−H12A···Br2	0.88	2.58	3.448(11)	168
	N12−H12A···Cl2	0.88	2.45	3.301(19)	164
	N12−H12B···Br1[k]	0.88	2.47	3.336(16)	169
	N12−H12B···Cl1[k]	0.88	2.50	3.38(4)	171
	N21−H21C···Br1[l]	0.91	2.69	3.484(15)	147

	N21−H21C···Cl1[l]	0.91	2.62	3.42(4)	147
	N21−H21D···Br1[m]	0.91	2.64	3.435(15)	147
	N21−H21D···C1[m]	0.91	2.63	3.43(4)	147
	N22−H22C···Br2[l]	0.91	2.62	3.400(11)	144
	N22−H22C···Cl2[l]	0.91	2.50	3.289(19)	146
	N22−H22D···Br2[m]	0.91	2.61	3.385(11)	144
	N22−H22D···Cl2[m]	0.91	2.59	3.355(19)	142
	O1W−H1WA···O1[n]	0.84(5)	1.97(5)	2.806(7)	173(8)
	N1−H1A···I1[o]	0.88	2.88	3.756(6)	173
2c$_{LT}$	N1−H1B···I1[p]	0.88	2.88	3.676(6)	151
	O1W−H1WB···I1[r]	0.86(6)	2.71(9)	3.461(5)	147(7)
	N2−H2D···I1[s]	0.91	2.97	3.762(6)	147
	N1−H1A···I1[t]	0.86	2.88	3.717(4)	166
	N1−H1B···I1[u]	0.86	2.89	3.690(4)	156
2c$_{RT}$	O1W−H1WB···I1[t]	0.87(7)	2.11(7)	2.907(6)	157(6)
	O1W−H1WB···I1	0.86(5)	2.76(6)	3.598(5)	166(7)

[a] 1/2+y,x,1/4+z; [b] 1-x,1-y,z; [c] y,1/2-x,1/4+z; [d] 1/2-y,1-x,1/4+z; [e]1/2-x,1/2+y,z; [f] 1-y,-1/2+x,1/4+z; [g] 1/2+x,1/2-y,z; [h] -1/2+x,3/2-y,z; [i] 2-x,1-y,z; [j] y,-1/2+x,-1/4+z ; [k] y,3/2-x,1/4+z ; [l]3/2-x,-1/2+y,z; [m]2-x,1-y,z; [n]1/2+x,2-y,z; [o]x,1+y,z; [p]-x,1/2+y,1/2-z ;[r]1/2+x,1-y,z ;[s]-1/2+x,1-y,z, [t] 1/2+x,y,5/2-z ; [u] 1-x,1-y,2-z

Table S10. Distances ([Å]) and angles ([°]) within the polyhedra of copper coordination spheres in the crystal structures of **3a** and **3b.**

Bond lengths [Å]

	3a	**3b**
Cu1–Cl/ Cu1–Cl^{i}	2.8282(3)	2.840(15)
Cu1–Br^{ii}		2.941(4)
Cu1–O1 / Cu1–O1^{i}	1.9912(8)	1.9907(15)
Cu1–N2 / Cu1–N2^{i}	1.9809(10)	1.9707(18)
Bond angles [°]		
Cl–Cu1–O1	87.06(2)	94.9(3)
Br–Cu1–O1		92.64(9)
Cl–Cu1–N2 / Cl^{i}–Cu1–N2^{i}	94.33(3)	86.0(3)
Br–Cu1–N2		84.65(10)
Cl–Cu1–Cl^{i}	180.00	180.00
Br1–Cu1–Br1^{ii}		180
Cl–Cu1–O1^{i} / Cl^{i}–Cu1–O1	92.94(2)	85.1(3)
Br–Cu1–O1^{i}		92.64(9)
Cl–Cu1–N2^{i} / Cl1^{i}–Cu1–N2	85.67(3)	94.0(3)
Br–Cu1–N2^{i} / Br^{i}–Cu1–N2		95.35(10)
O1–Cu1–N2 / O1^{i}–Cu1–N2^{i}	82.57(3)	82.4(2)
Br1^{i}–Cu1–O1		93.04(14)
O1–Cu1–O1^{i}	180.00	
O1–Cu1–O1^{ii}		180.00
O1–Cu1–N2^{i} / O1^{i}–Cu1–N2	97.43(3)	97.38(7)
Br1^{i}–Cu1–N2		87.36(9)
N2–Cu1–N2^{i}	180.00	
Br1^{ii}–Cu1–O1^{ii}		86.96(14)
Br1^{ii}–Cu1–N2^{ii}		95.1(2)
O1^{ii}–Cu1–N2^{ii}		82.4(2)

^{i} 2-x,-y,1-z; ^{ii} -x, -y, 2-z

Table S11. Geometry of selected intermolecular hydrogen bonds ([Å],[°]) for compounds **3a** and **3b.**

	D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	D–H···A [°]
3a	N1–H1A···Cl[a]	0.824(18)	2.474(18)	3.2800(11)	166.2(14)
	N1–H1B···Cl[b]	0.814(17)	2.552(16)	3.3506(11)	167.1(18)
	N2–H2C···Cl[c]	0.848(19)	2.522(19)	3.3384(10)	162(2)
	N2–H2D···Cl[d]	0.96(2)	2.74(2)	3.3282(10)	119.9(15)
3b	N1–H1A···**Br**[e]	0.86	2.52	3.344(5)	160
	N1–H1A···Cl[e]	0.86	2.60	3.407(18)	158
	N1–H1B···Br[f]	0.86	2.61	3.452(4)	165
	N2–H2C···Cl[f]	0.86	2.59	3.419(17)	162
	N2–H2C···Br	0.89	2.90	3.384(4)	116
	N2–H2D···Br[g]	0.89	2.59	3.409(5)	154
	N2–H2D···Cl[g]	0.89	2.53	3.339(18)	151

[a] 1/2+x,-1/2-y,-1/2+z; [b] 2-x,-1-y,1-z [c]1/2+x,-1/2-y,1/2+z; [d] 2-x,-y,1-z, [e] 1/2-x,1/2+y,3/2-z; [f]x,1+y,z;
[g] 1/2-x,1/2+y,1/2-z

Table S12. Distances ([Å]) and angles ([°]) within the polyhedra of copper coordination spheres in the crystal structure of **3c**.

Bond lengths [Å]	
Cu1^{i}–I1	3.1632(8)
Cu1–I3	3.2963(8)
Cu1–O11	1.953(4)
Cu1–O12	1.958(4)
Cu1–N21	1.996(5)
Cu1–N22	1.981(5)
Cu2–I1	2.6442(8)
Cu2–I2	2.7228(9)
Cu2^{ii}–I2	2.6696(12)
Cu2–I3	2.6374(9)
Bond angles [°]	
I3–Cu1–O12	89.36(12)
I3–Cu1–N21	87.30(14)
I3–Cu1–N22	86.75(15)
I1^{iii}–Cu1–I3	173.99(3)
O11–Cu1–O12	89.26(16)
O11–Cu1–N21	87.30(14)
O11–Cu1–N22	171.71(19)
I1^{iii}–Cu1–O11	96.97(12)
O12–Cu1–N21	172.75(19)
O12–Cu1–N22	84.06(18)
I1^{iii}–Cu1–O12	93.63(12)
N21–Cu1–N22	102.16(19)
I1^{iii}–Cu1–N21	90.30(15)
I1^{iii}–Cu1–N22	88.38(15)
I1–Cu2–I2	108.13(3)
I1–Cu2–I3	108.45(3)
I1–Cu2–I2^{ii}	112.86(3)
I2–Cu2–I3	110.57(4)
I2–Cu2–I2^{ii}	112.86(3)
I2^{ii}–Cu2–I3	109.74(3)

^{i}-1+x,1+y,z; ^{ii} -x,1-y,1-z, ^{iii} 1+x,-1+y,z

Table S13. Geometry of selected intermolecular hydrogen bonds ([Å],[°]) for compound 3c.

	D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	D–H···A [°]
	N11–H11A···O11[a]	0.86	2.57	3.266(7)	139
	N11–H11B···I1[b]	0.86	2.81	3.627(6)	159
	N11–H11B···I1[c]	0.86	3.02	3.863(5)	167
3c	N11–H11B···I1[d]	0.86	3.05	3.884(6)	166
	N11–H11B···I1[e]	0.89	2.76	3.627(5)	167
	N11–H11B···I1[f]	0.89	2.95	3.707(5)	144
	N11–H11B···I1[d]	0.97	2.99	3.808(5)	143

[a] 1-x,-y,-z; [b] x,-1+y,z; [c] 1-x,1-y,-z; [d] 1+x,y,z;[e] 1+x,-1+y,z; [f]1-x,-y,1-z

Table S14. Conformations of five membered chelate glycinamide rings in compounds **1a**, **1b**, **1c**, **2a**,

Compound	5 membered ring / closest pucker description	5 membered ring / closest pucker description
1a	Co1–O11–C11–C21–N21 / Envelope on N21	Co1–O12–C12–C22–N22 / Half chair (twisted on C22–N22)
1b	Co1–O11–C11–C21–N21 / Half chair (twisted on C21–N21)	Co1–O12–C12–C22–N22 / Envelope on N22
1c	Co1–O1–C1–C2–N2 / Planar	Co1–O1^{i}–C1^{i} –C2^{i} –N2^{i} / Planar
2a	Ni1–O11–C11–C21–N21 / Half chair (twisted on C21–N21)	Ni1–O12–C12–C22–N22 / Envelope on N22
2b	Ni1–O11–C11–C21–N21 / Envelope on N21	Ni1–O12–C12–C22–N22 / Half chair (twisted on C22–N22)
2c$_{LT}$	Ni1–O1–C1–C2–N2 / Half chair (twisted on N2–Ni1)	Ni1–O1^{ii}–C1^{ii}–C2^{ii}–N2^{ii} / Half chair (twisted on N2^{ii} –Ni1)
2c$_{RT}$	Ni1–O1–C1–C2–N2 / Planar	Ni1–O1^{iii}–C1^{iii}–C2^{iii}–N2^{iii} / Planar
3a	Cu1–O1–C1–C2–N2/ Half chair (twisted on N2–Cu1)	Cu1–O1^{iv}–C1^{iv}–C2^{iv}–N2^{iv} / Half chair (twisted on N2^{iv}–Cu1)
3b	Cu1–O1–C1–C2–N2/ Half chair (twisted on N2–Cu1)	Cu1–O1^{v}–C1^{v}–C2^{v}–N2^{v} / Half chair (twisted on N2^{v}–Cu1)
3c	Cu1–O11–C11–C21–N21 / Half chair (twisted on C21–N21)	Cu1–O12–C12–C22–N22 / Envelope on N22

^{i} x,1/2-y,z; ^{ii} 1/2-x,y,1-z; ^{iii} x,3/2-y,z; ^{iv} 2-x,-y,1-z, ^{v} 1-x, 1-y, 1-z

2b, **2c$_{LT}$**, **2c$_{RT}$**, **3a**, **3b** and **3c**.

Table S15. The principal *g*-values obtained from the spectral simulations, together with the parameter used for the simulations: $\mathbf{g}_{strain}$ and linewidths l_w.

Complex	**g = [g$_x$ g$_y$ g$_z$]**	**g$_{strain}$**	***l$_w$* / mT**	***T* / K**
1a	[5.3 4.2 2.2]	[0 0 0]	210	78
			130	40
1b	[6.5 3.5 2.2]	[0 0 0]	180	78
			100	40
3a	[2.00 2.08 2.21]	[0.25 0.0 0.0]	3	297
		[0.25 0.0 0.0]	4	78
3b	[2.00 2.08 2.21]	[0.16 0.0 0.04]	3	297
		[0.7 0.0 0.04]	8	78

Biological activity

The experiments were carried out on three human cell lines: HCT 116 (colon carcinoma), H 460 (lung carcinoma) and MCF-7 (breast carcinoma) according to the previously published experimental procedure.[21]

Briefly, the cells were grown in DMEM medium with the addition of 10% fetal bovine serum (FBS), 2 mM L-glutamine, 100 U/mL penicillin and 100 µg/mL streptomycin, and cultured as monolayers at 37 °C in a humidified atmosphere with 5% CO_2. Cells were seeded onto a standard 96-well microtiter plates and left to attach for 24 h. Next day, test compounds were added in five serial 10-fold dilutions. The cell viability was evaluated after 72 h of incubation, using MTT assay, a colorimetric assay system, which detects dehydrogenase activity in viable cells. The absorbance, measured on a microplate reader at 570 nm, is directly proportional to the cell viability. The percentage of growth (PG) of the cell lines was calculated. Obtained results are expressed as IC_{50} value which stands for the concentration of the compound necessary for 50% of growth inhibition. The IC_{50} values were calculated from concentration-response curve using linear regression analysis by fitting the test concentrations that give PG values above and below the reference value (i.e. 50%). If all of the tested concentrations produce PGs exceeding the respective reference level of effect, then the highest tested concentration is assigned as the default value by a ">" sign. Each test was performed in quadruplicate in at least two individual experiments.

Table S16. IC_{50} values for compounds **1a** and **3a**

Compound	IC_{50}[a] / 10^{-6} mol dm^{-3}		
	MCF-7	HCT116	H 460
1a	11±5	≥100	≥100
3a	13±0.1	≥100	≥100

[a]IC_{50}; the concentration that causes 50% growth inhibition