SUPPORTING INFORMATION

to the paper: “Valence tautomeric interconversion of bis-dioxolene cobalt complex with imino-pyridine functionalized by TEMPO moiety in solid solutions with isostructural nickel analogue. Phase transitions and monocrystals destruction”, by Alexey A. Zolotukhin, Michael P. Bubnov, Georgy K. Fukin, Roman V. Rumyantcev, Artem S. Bogomyakov.

Table S1. X-ray fluorescence analysis data for solid solutions of complexes **1** and **2**.

Initial Co:Ni ratio	1:1 (50.0:50.0%)	1:2 (33.3:66.7%)	1:4 (20.0:80.0%)	1:8 (11.1:89.9%)
Experimental ratio	47.85: 52.15	39.695:60.305	19.60:80.40	10.80:89.20

Table S2 Details of crystallographic, collection and refinement data for complexes **1***, **2** and their solid solutions 1:1, 1:4 and 1:8.

Complex	**1** (Co)*	**1**:**1**	**1**:**4**	**1**:**4**
Empirical formula	$C_{43}H_{62}CoN_3O_5$	$C_{43}H_{62}Co_{0.50}N_3Ni_{0.50}O_5$	$C_{43}H_{62}Co_{0.20}N_3Ni_{0.80}O_5$	$C_{43}H_{62}Co_{0.20}N_3Ni_{0.80}O_5$
Formula weight	759.88	759.77	759.71	759.71
Temperature [K]	240(2)	240(2)	240(2)	200(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions				
a[Å]	10.7483(2)	10.7499(2)	10.7509(2)	10.7388(2)
b[Å]	15.8276(4)	15.7050(3)	15.6732(3)	15.6003(2)
c[Å]	26.6639(6)	26.8932(6)	26.9924(6)	26.9877(5)
β[°]	101.5058(10)	101.056(2)	100.866(2)	100.788(2)
Volume [Å^3]	4444.90(17)	4456.03(16)	4466.70(16)	4441.30(13)
Z	4	4	4	4
Calculated density [Mg/m^3]	1.136	1.133	1.130	1.136
Absorption coefficient [mm^{-1}]	0.429	0.453	0.467	0.469
F(000)	1632	1634	1635	1635
Crystal size [mm^3]	0.50×0.30×0.16	0.42×0.33×0.19	0.49×0.36×0.28	0.49×0.36×0.28
ϑ [°]	2.323 – 27.998	2.016 – 27.485	2.982 – 26.022	2.984 – 26.021
Reflections collected / unique	52187 / 10731	60877 / 10211	59856 / 8800	60523 / 8752
R(int)	0.0395	0.0296	0.0369	0.0354
Final R indices [I>2sigma(I)]	R_1=0.0450, wR_2=0.1106	R_1=0.0351, wR_2=0.0836	R_1=0.0353, wR_2=0.0820	R_1=0.0328, wR_2=0.0760
R indices (all data)	R_1=0.0637, wR_2=0.1186	R_1=0.0538, wR_2=0.0938	R_1=0.0491, wR_2=0.0893	R_1=0.0435, wR_2=0.0815
S	1.024	1.032	1.020	1.024
Largest diff. peak and hole [e/Å^3]	0.341/-0.518	0.302/-0.255	0.264/-0.218	0.272/-0.229

Complex	**1**:**4**	**1**:**8**	**1**:**8**	**1**:**8**
Empirical formula	$C_{43}H_{62}Co_{0.20}N_3Ni_{0.80}O_5$	$C_{43}H_{62}Co_{0.11}N_3Ni_{0.89}O_5$	$C_{43}H_{62}Co_{0.11}N_3Ni_{0.89}O_5$	$C_{43}H_{62}Co_{0.11}N_3Ni_{0.89}O_5$
Formula weight	759.71	759.69	759.69	759.69
Temperature [K]	150(2)	240(2)	200(2)	130(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions				
a[Å]	10.7123(2)	10.7610(5)	10.7426(3)	10.70656(13)
b[Å]	15.4635(2)	15.6753(6)	15.6134(4)	15.45339(16)
c[Å]	26.9889(5)	27.0721(11)	27.0073(7)	26.9829(4)
β[°]	100.441(2)	100.755(4)	100.807(2)	100.6212(12)
Volume [Å^3]	4396.68(13)	4486.3(3)	4449.6(2)	4387.90(9)
Z	4	4	4	4
Calculated density [Mg/m^3]	1.148	1.125	1.134	1.150
Absorption coefficient [mm^{-1}]	0.474	0.469	0.473	0.480
F(000)	1635	1636	1636	1636
Crystal size [mm^3]	0.49×0.36×0.28	0.40×0.40×0.20	0.40×0.40×0.20	0.60×0.40×0.20
ϑ [°]	2.984 – 26.022	3.005 – 30.000	2.983 – 29.999	2.990 – 29.999
Reflections collected / unique	56588 / 8652	89592 / 13064	86718 / 12948	85866 / 12766
R(int)	0.0361	0.0835	0.0601	0.0596
Final R indices [I>2sigma(I)]	R_1=0.0314, wR_2=0.0711	R_1=0.0526, wR_2=0.0905	R_1=0.0437, wR_2=0.0895	R_1=0.0436, wR_2=0.0900
R indices (all data)	R_1=0.0397, wR_2=0.0749	R_1=0.1117, wR_2=0.1036	R_1=0.0752, wR_2=0.0989	R_1=0.0742, wR_2=0.0994
S	1.031	0.987	1.040	1.041
Largest diff. peak and hole [e/Å^3]	0.297/-0.229	0.230/-0.239	0.263/-0.281	0.258/-0.297

Complex	**2** (Ni)	**2** (Ni)
Empirical formula	$C_{43}H_{62}N_3NiO_5$	$C_{43}H_{62}N_3NiO_5$
Formula weight	759.66	759.66
Temperature [K]	240(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions		
a[Å]	10.7157(5)	10.7053(2)
b[Å]	15.5691(8)	15.4760(2)
c[Å]	26.9871(13)	26.9999(5)
β[°]	100.6894(9)	100.978(2)
Volume [Å^3]	4424.2(4)	4391.36(13)
Z	4	4
Calculated density [Mg/m^3]	1.140	1.149
Absorption coefficient [mm^{-1}]	0.481	0.485
F(000)	1636	1636
Crystal size [mm^3]	0.24×0.22×0.10	0.49×0.22×0.13
ϑ [°]	2.236 – 26.142	2.998 – 29.999
Reflections collected / unique	43915 / 8811	26975 / 12783
R(int)	0.1506	0.0425
Final R indices [I>2sigma(I)]	R_1=0.0462, wR_2=0.1154	R_1=0.0464, wR_2=0.0876
R indices (all data)	R_1=0.0624, wR_2=0.1246	R_1=0.0845, wR_2=0.0971
S	1.043	0.978
Largest diff. peak and hole [e/Å^3]	0.330/-0.597	0.397/-0.371

Table S3. The selected bonds lengths [Å] and angles [deg] in «pure» cobalt (**1**)* and nickel (**2**) complexes and their solid solutions 1:1, 1:4 and 1:8 at different temperatures (T).

Bond, Å	**1** (Co)	**1**:**1**		**1**:**4**	
M, T	Co, 240 K	Co, 240 K	Ni, 240 K	Co, 240 K	Ni, 240 K
M(1)-O(1)	2.0271(12)	2.025(2)	2.0226(14)	2.030(5)	2.0231(12)
M(1)-O(2)	2.0329(13)	2.021(2)	2.0323(15)	2.022(5)	2.0275(13)
M(1)-O(3)	2.0062(12)	2.004(2)	2.0065(14)	1.998(5)	2.0050(12)
M(1)-O(4)	2.0659(13)	2.058(2)	2.0553(15)	2.060(5)	2.0557(13)
M(1)-N(1)	2.1080(14)	2.085(2)	2.0881(16)	2.077(5)	2.0825(15)
M(1)-N(2)	2.1443(15)	2.135(2)	2.1238(16)	2.128(5)	2.1222(15)
O(1)-C(1)	1.279(2)	1.2830(18)		1.2827(19)	
O(2)-C(2)	1.275(2)	1.2762(18)		1.2785(19)	
C(1)-C(2)	1.470(2)	1.468(2)		1.468(2)	
O(3)-C(15)	1.274(2)	1.2786(18)		1.278(2)	
O(4)-C(16)	1.276(2)	1.2806(19)		1.281(2)	
C(15)-C(16)	1.464(2)	1.463(2)		1.462(2)	
O(5)-N(3)	1.275(2)	1.279(2)		1.279(2)	
Angle, deg	**1** (Co)	**1**:**1**		**1**:**4**	
M, T	Co, 240 K	Co, 240 K	Ni, 240 K	Co, 240 K	Ni, 240 K
O(1)-M(1)-O(2)	79.35(5)	80.29(8)	80.06(5)	80.35(18)	80.38(5)
O(1)-M(1)-O(3)	169.94(5)	170.76(11)	170.51(7)	170.8(3)	170.80(5)
O(1)-M(1)-O(4)	92.46(5)	92.42(9)	92.55(6)	92.3(2)	92.60(5)
O(1)-M(1)-N(1)	100.64(5)	99.20(9)	99.18(6)	98.6(2)	98.61(5)
O(1)-M(1)-N(2)	93.15(5)	93.07(9)	93.47(6)	93.2(2)	93.53(5)
O(2)-M(1)-O(3)	95.48(5)	94.71(9)	94.26(6)	94.4(2)	93.99(5)
O(2)-M(1)-O(4)	89.86(6)	89.00(9)	88.74(6)	88.5(2)	88.47(5)
O(2)-M(1)-N(1)	92.16(6)	92.61(9)	92.19(6)	92.7(2)	92.38(6)
O(2)-M(1)-N(2)	165.72(5)	167.48(11)	167.40(7)	168.1(3)	168.10(5)
O(3)-M(1)-O(4)	78.82(5)	79.66(8)	79.65(5)	79.96(18)	79.91(5)
O(3)-M(1)-N(1)	88.09(5)	88.73(9)	88.57(6)	89.2(2)	88.83(5)
O(3)-M(1)-N(2)	93.66(5)	93.23(9)	93.49(6)	93.3(2)	93.26(5)
O(4)-M(1)-N(1)	166.89(5)	168.38(11)	168.22(7)	169.1(3)	168.74(5)
O(4)-M(1)-N(2)	102.69(6)	101.96(9)	102.42(6)	101.8(2)	102.09(5)
N(1)-M(1)-N(2)	77.18(6)	77.89(8)	78.08(6)	78.35(18)	78.34(6)

Bond, Å	**1**:**4**		**1**:**4**		**1**:**8**	
M, T	Co, 200 K	Ni, 200 K	Co, 150 K	Ni, 150 K	Co, 240 K	Ni, 240 K
M(1)-O(1)	2.022(5)	2.0197(11)	1.998(4)	2.0032(11)	2.037(10)	2.0258(12)
M(1)-O(2)	2.015(5)	2.0210(12)	1.996(5)	2.0047(11)	2.023(11)	2.0293(13)
M(1)-O(3)	1.998(5)	2.0010(11)	1.990(4)	1.9849(10)	1.996(10)	2.0065(12)
M(1)-O(4)	2.054(5)	2.0533(12)	2.038(4)	2.0352(11)	2.065(10)	2.0593(13)
M(1)-N(1)	2.075(5)	2.0764(13)	2.057(4)	2.0590(12)	2.077(10)	2.0839(15)
M(1)-N(2)	2.121(5)	2.1158(14)	2.106(5)	2.0973(13)	2.128(11)	2.1221(15)
O(1)-C(1)	1.2845(18)		1.2878(17)		1.2908(19)	
O(2)-C(2)	1.2826(18)		1.2875(17)		1.2822(19)	
C(1)-C(2)	1.469(2)		1.468(2)		1.470(2)	
O(3)-C(15)	1.2795(18)		1.2830(17)		1.282(2)	
O(4)-C(16)	1.2805(19)		1.2856(18)		1.283(2)	
C(15)-C(16)	1.466(2)		1.465(2)		1.466(3)	
O(5)-N(3)	1.280(2)		1.2803(18)		1.281(2)	
Angle, deg	**1**:**1**		**1**:**4**		**1**:**8**	
M, T	Co, 200 K	Ni, 200 K	Co, 150 K	Ni, 150 K	Co, 240 K	Ni, 240 K
O(1)-M(1)-O(2)	80.77(17)	80.69(4)	81.80(17)	81.44(4)	80.5(4)	80.59(5)
O(1)-M(1)-O(3)	171.3(3)	171.12(5)	172.0(3)	171.84(5)	170.9(6)	171.00(5)
O(1)-M(1)-O(4)	92.54(19)	92.62(5)	92.66(18)	92.57(4)	92.0(4)	92.48(5)
O(1)-M(1)-N(1)	98.35(19)	98.38(5)	97.87(19)	97.65(5)	98.4(4)	98.50(5)
O(1)-M(1)-N(2)	93.12(19)	93.35(5)	92.90(18)	93.00(5)	93.0(4)	93.54(5)
O(2)-M(1)-O(3)	94.1(2)	93.87(5)	93.53(19)	93.39(4)	94.4(5)	93.92(5)
O(2)-M(1)-O(4)	88.45(19)	88.31(5)	88.17(18)	87.99(5)	88.4(4)	88.36(5)
O(2)-M(1)-N(1)	92.5(2)	92.31(5)	92.49(19)	92.18(5)	92.8(4)	92.37(5)
O(2)-M(1)-N(2)	168.3(3)	168.32(5)	169.2(2)	168.92(5)	168.5(6)	168.50(5)
O(3)-M(1)-O(4)	80.20(17)	80.15(4)	80.71(16)	80.88(4)	80.3(4)	80.17(5)
O(3)-M(1)-N(1)	88.89(18)	88.79(5)	88.74(18)	88.82(4)	89.3(4)	88.80(5)
O(3)-M(1)-N(2)	93.10(19)	93.19(5)	92.73(18)	93.12(5)	93.2(4)	93.07(5)
O(4)-M(1)-N(1)	169.1(3)	168.94(5)	169.4(2)	169.69(5)	169.6(6)	168.97(5)
O(4)-M(1)-N(2)	101.8(2)	102.06(5)	101.53(19)	101.89(5)	101.5(5)	101.85(5)
N(1)-M(1)-N(2)	78.45(17)	78.55(5)	78.85(16)	79.01(5)	78.7(4)	78.64(6)

Bond, Å	**1**:**8**		**1**:**8**		**2** (Ni)	**2** (Ni)
M, T	Co, 200 K	Ni, 200 K	Co, 130 K	Ni, 130 K	Ni, 240 K	Ni, 100 K
M(1)-O(1)	2.023(8)	2.0234(10)	2.010(8)	2.0121(10)	2.0176(14)	2.0281(11)
M(1)-O(2)	1.990(9)	2.0244(11)	1.989(10)	2.0225(11)	2.0204(16)	2.0268(12)
M(1)-O(3)	2.005(8)	2.0050(10)	1.996(8)	1.9951(10)	2.0000(14)	2.0085(10)
M(1)-O(4)	2.070(8)	2.0572(11)	2.054(8)	2.0414(11)	2.0465(15)	2.0589(11)
M(1)-N(1)	2.066(8)	2.0791(12)	2.049(8)	2.0612(12)	2.0727(17)	2.0771(13)
M(1)-N(2)	2.147(9)	2.1152(13)	2.143(10)	2.1117(13)	2.1119(18)	2.1121(14)
O(1)-C(1)	1.2856(17)		1.2821(17)		1.279(2)	1.2862(19)
O(2)-C(2)	1.2811(17)		1.2730(17)		1.273(2)	1.2807(18)
C(1)-C(2)	1.473(2)		1.470(2)		1.465(3)	1.475(2)
O(3)-C(15)	1.2810(17)		1.2728(17)		1.272(2)	1.2801(18)
O(4)-C(16)	1.2841(17)		1.2791(18)		1.273(3)	1.2854(18)
C(15)-C(16)	1.467(2)		1.453(2)		1.471(3)	1.474(2)
O(5)-N(3)	1.2790(19)		1.2726(19)		1.277(3)	1.2828(19)
Angle, deg	**1**:**1**		**1**:**4**		**2** (Ni)	**2** (Ni)
M, T	Co, 200 K	Ni, 200 K	Co, 150 K	Ni, 150 K	Ni, 240 K	Ni, 100 K
O(1)-M(1)-O(2)	81.5(3)	80.66(4)	81.7(3)	80.80(4)	80.61(6)	80.91(4)
O(1)-M(1)-O(3)	171.4(5)	171.13(4)	171.5(5)	171.15(4)	170.93(6)	171.55(4)
O(1)-M(1)-O(4)	92.1(3)	92.51(4)	92.5(3)	92.82(4)	92.59(6)	92.80(4)
O(1)-M(1)-N(1)	98.8(4)	98.33(4)	98.5(4)	98.04(4)	98.20(6)	98.13(5)
O(1)-M(1)-N(2)	92.5(3)	93.45(4)	92.4(4)	93.29(4)	93.59(6)	93.15(5)
O(2)-M(1)-O(3)	95.0(4)	93.88(4)	94.8(4)	93.76(4)	93.76(6)	93.85(4)
O(2)-M(1)-O(4)	88.6(3)	88.06(5)	88.9(3)	88.37(5)	88.29(6)	88.03(5)
O(2)-M(1)-N(1)	93.8(4)	92.44(5)	93.5(4)	92.11(5)	92.39(7)	92.27(5)
O(2)-M(1)-N(2)	169.2(5)	168.49(5)	169.3(5)	168.53(4)	168.60(6)	168.50(5)
O(3)-M(1)-O(4)	80.0(3)	80.26(4)	79.7(3)	79.99(4)	80.07(6)	80.33(4)
O(3)-M(1)-N(1)	89.2(3)	88.83(4)	89.4(3)	89.08(4)	89.09(6)	88.65(5)
O(3)-M(1)-N(2)	92.2(3)	93.09(5)	92.3(4)	93.23(5)	93.13(6)	93.12(5)
O(4)-M(1)-N(1)	169.1(4)	169.09(4)	169.0(5)	169.06(5)	169.16(6)	168.98(5)
O(4)-M(1)-N(2)	100.6(4)	102.14(5)	100.3(4)	101.80(5)	101.84(7)	102.16(5)
N(1)-M(1)-N(2)	78.1(3)	78.56(5)	78.5(3)	78.92(5)	78.65(7)	78.76(5)

Table S4. Selected topological characteristics in CP(3, –1), corresponding to intermolecular interactions in crystals of «pure» cobalt (**1**)* and nickel (**2**) complexes and their solid solution 1:8 at 240 K.

Bond	ρ(r), a.u.	$\nabla^2\rho(r)$, a.u.	v(r), a.u.	h_e, a.u.	E_{EML}, kcal/mol**
Ni					
O…H					
O(5)…H(32)	0.013	0.054	-0.009	0.002	2.75
H(32)…O(5)	0.013	0.054	-0.009	0.002	2.75
O(5)…H(34)	0.004	0.019	-0.002	0.001	0.70
H(34)…O(5)	0.004	0.019	-0.002	0.001	0.70
C…H					
H(31)…C(1)	0.006	0.029	-0.003	0.002	1.07
C(14)…H(30)	0.004	0.018	-0.002	0.001	0.68
H(28A)…C(34)	0.004	0.019	-0.002	0.001	0.68
H(30)…C(14)	0.004	0.018	-0.002	0.001	0.68
C(34)…H(28A)	0.004	0.019	-0.002	0.001	0.68
C(4)…H(12A)	0.004	0.017	-0.002	0.001	0.64
H(12A)…C(4)	0.004	0.017	-0.002	0.001	0.64
H(14B)…C(19)	0.004	0.014	-0.002	0.001	0.56
C(19)…H(14B)	0.004	0.014	-0.002	0.001	0.56
H(8B)…C(14)	0.002	0.009	-0.001	0.001	0.31
C(14)…H(8B)	0.002	0.009	-0.001	0.001	0.31
H(39B)…C(41)	0.001	0.006	-0.001	0.0005	0.18
C…C					
C(29)…C(30)	0.005	0.016	-0.002	0.001	0.73
C(30)…C(29)	0.005	0.016	-0.002	0.001	0.73
H…H					
H(28B)…H(34)	0.005	0.020	-0.002	0.001	0.77
H(34)…H(28B)	0.005	0.020	-0.002	0.001	0.77
H(9A)…H(27B)	0.003	0.020	-0.002	0.001	0.68
H(23B)…H(42C)	0.004	0.020	-0.002	0.001	0.68
H(27B)…H(9A)	0.003	0.020	-0.002	0.001	0.68
H(42C)…H(23B)	0.004	0.020	-0.002	0.001	0.68
H(10A)…H(43B)	0.003	0.020	-0.002	0.001	0.67
H(43B)…H(10A)	0.003	0.020	-0.002	0.001	0.67
H(27C)…H(30)	0.004	0.017	-0.002	0.001	0.62
H(30)…H(27C)	0.004	0.017	-0.002	0.001	0.62
H(19)…H(36A)	0.002	0.020	-0.002	0.002	0.58
H(36A)…H(19)	0.002	0.020	-0.002	0.002	0.58
H(10C)…H(24C)	0.003	0.015	-0.002	0.001	0.52
H(24C)…H(10C)	0.003	0.015	-0.002	0.001	0.52
H(4)…H(13C)	0.003	0.015	-0.002	0.001	0.51
H(13C)…H(4)	0.003	0.015	-0.002	0.001	0.51
H(14A)…H(31)	0.003	0.014	-0.002	0.001	0.50
H(31)…H(14A)	0.003	0.014	-0.002	0.001	0.50
H(26C)…H(41A)	0.003	0.013	-0.001	0.001	0.44
H(41A)…H(26C)	0.003	0.013	-0.001	0.001	0.44
H(8B)…H(12C)	0.003	0.012	-0.001	0.001	0.43
H(12C)…H(8B)	0.003	0.012	-0.001	0.001	0.43
H(5)…H(42A)	0.003	0.011	-0.001	0.001	0.40
H(42A)…H(5)	0.003	0.011	-0.001	0.001	0.40
H(19)…H(40B)	0.002	0.012	-0.001	0.001	0.39

H(40B)…H(19)	0.002	0.012	-0.001	0.001	0.39
H(24A)…H(26A)	0.002	0.012	-0.001	0.001	0.37
H(26A)…H(24A)	0.002	0.012	-0.001	0.001	0.37
H(13B)…H(18)	0.002	0.010	-0.001	0.001	0.34
H(18)…H(13B)	0.002	0.010	-0.001	0.001	0.34
H(23B)…H(35)	0.002	0.011	-0.001	0.001	0.34
H(35)…H(23B)	0.002	0.011	-0.001	0.001	0.34
H(4)…H(43C)	0.002	0.009	-0.001	0.001	0.30
H(27B)…H(29)	0.002	0.009	-0.001	0.001	0.30
H(29)…H(27B)	0.002	0.009	-0.001	0.001	0.30
H(43C)…H(4)	0.002	0.009	-0.001	0.001	0.30
H(28A)…H(36A)	0.002	0.007	-0.001	0.001	0.24
H(36A)…H(28A)	0.002	0.007	-0.001	0.001	0.24
H(9B)…H(26B)	0.001	0.007	-0.001	0.001	0.22
H(26B)…H(9B)	0.001	0.007	-0.0007	0.0005	0.22
H(24A)…H(28C)	0.001	0.007	-0.001	0.001	0.21
H(28C)…H(24A)	0.001	0.007	-0.001	0.001	0.21
H(24B)…H(40A)	0.001	0.007	-0.001	0.001	0.20
H(40A)…H(24B)	0.001	0.007	-0.001	0.001	0.20
H(12C)…H(22B)	0.001	0.005	-0.001	0.0004	0.16
H(22B)…H(12C)	0.001	0.005	-0.001	0.0004	0.16
H(26B)…H(40C)	0.001	0.004	-0.0004	0.0003	0.11
H(40C)…H(26B)	0.001	0.004	-0.0004	0.0003	0.11
H(9C)…H(32)	0.001	0.003	-0.0003	0.0003	0.10
H(32)…H(9C)	0.001	0.003	-0.0003	0.0003	0.10
H(10B)…H(40C)	0.001	0.003	-0.0003	0.0002	0.08
H(40C)…H(10B)	0.001	0.003	-0.0003	0.0002	0.08
Total energy					~36
Co					
O…H					
O(5)…H(32)	0.012	0.049	-0.008	0.002	2.47
H(32)…O(5)	0.012	0.049	-0.008	0.002	2.47
C…H					
C(1)…H(31)	0.006	0.030	-0.004	0.002	1.18
H(31)…C(1)	0.006	0.030	-0.004	0.002	1.18
C(34)…H(28A)	0.004	0.019	-0.002	0.001	0.69
H(28A)…C(34)	0.004	0.019	-0.002	0.001	0.69
H(30)…C(14)	0.004	0.017	-0.002	0.001	0.67
C(14)…H(30)	0.004	0.017	-0.002	0.001	0.67
C(4)…H(12A)	0.004	0.017	-0.002	0.001	0.62
H(12A)…C(4)	0.004	0.017	-0.002	0.001	0.62
H(14B)…C(19)	0.004	0.013	-0.002	0.001	0.52
C(19)…H(14B)	0.004	0.013	-0.002	0.001	0.52
C(4)…H(43C)	0.003	0.010	-0.001	0.001	0.35
H(43C)…C(4)	0.003	0.010	-0.001	0.001	0.35
H(8B)…C(14)	0.002	0.009	-0.001	0.001	0.31
C(14)…H(8B)	0.002	0.009	-0.001	0.001	0.31
H(39B)…C(41)	0.001	0.005	-0.0004	0.0004	0.13
C(41)…H(39B)	0.001	0.005	-0.0004	0.0004	0.13
C…C					
C(29)…C(30)	0.005	0.016	-0.002	0.001	0.71
C(30)…C(29)	0.005	0.016	-0.002	0.001	0.71

H…H					
H(34)…H(28B)	0.004	0.019	-0.002	0.001	0.72
H(28B)…H(34)	0.004	0.019	-0.002	0.001	0.72
H(9A)…H(27B)	0.003	0.019	-0.002	0.001	0.61
H(27B)…H(9A)	0.003	0.019	-0.002	0.001	0.61
H(23B)…H(42C)	0.003	0.017	-0.002	0.001	0.59
H(42C)…H(23B)	0.003	0.017	-0.002	0.001	0.59
H(10A)…H(43B)	0.003	0.018	-0.002	0.001	0.58
H(43B)…H(10A)	0.003	0.018	-0.002	0.001	0.58
H(27C)…H(30)	0.004	0.016	-0.002	0.001	0.56
H(30)…H(27C)	0.004	0.016	-0.002	0.001	0.56
H(19)…H(36A)	0.002	0.018	-0.002	0.001	0.54
H(36A)…H(19)	0.002	0.018	-0.002	0.001	0.54
H(4)…H(13C)	0.003	0.015	-0.002	0.001	0.53
H(13C)…H(4)	0.003	0.015	-0.002	0.001	0.53
H(26C)…H(41A)	0.003	0.015	-0.002	0.001	0.52
H(41A)…H(26C)	0.003	0.015	-0.002	0.001	0.52
H(10C)…H(24C)	0.003	0.014	-0.002	0.001	0.51
H(24C)…H(10C)	0.003	0.014	-0.002	0.001	0.51
H(14A)…H(31)	0.003	0.014	-0.002	0.001	0.49
H(31)…H(14A)	0.003	0.014	-0.002	0.001	0.49
H(5)…H(42A)	0.003	0.012	-0.001	0.001	0.45
H(42A)…H(5)	0.003	0.012	-0.001	0.001	0.45
H(19)…H(40B)	0.002	0.012	-0.001	0.001	0.39
H(40B)…H(19)	0.002	0.012	-0.001	0.001	0.39
H(12C)…H(8B)	0.002	0.010	-0.001	0.001	0.34
H(8B)…H(12C)	0.002	0.010	-0.001	0.001	0.34
H(13B)…H(18)	0.002	0.010	-0.001	0.001	0.34
H(18)…H(13B)	0.002	0.010	-0.001	0.001	0.34
H(27B)…H(29)	0.002	0.010	-0.001	0.001	0.32
H(29)…H(27B)	0.002	0.010	-0.001	0.001	0.32
H(23B)…H(35)	0.002	0.010	-0.001	0.001	0.31
H(35)…H(23B)	0.002	0.010	-0.001	0.001	0.31
H(24A)…H(26A)	0.002	0.009	-0.001	0.001	0.30
H(26A)…H(24A)	0.002	0.009	-0.001	0.001	0.30
H(24A)…H(28C)	0.002	0.008	-0.001	0.001	0.25
H(28C)…H(24A)	0.002	0.008	-0.001	0.001	0.25
H(9B)…H(26B)	0.002	0.008	-0.001	0.001	0.24
H(26B)…H(9B)	0.002	0.008	-0.001	0.001	0.24
H(24B)…H(40A)	0.001	0.006	-0.001	0.001	0.17
H(40A)…H(24B)	0.001	0.006	-0.001	0.001	0.17
H(12C)…H(22B)	0.001	0.005	-0.001	0.000	0.16
H(22B)…H(12C)	0.001	0.005	-0.001	0.0004	0.16
H(10B)…H(40C)	0.001	0.005	-0.0004	0.0004	0.14
H(40C)…H(10B)	0.001	0.005	-0.0004	0.0004	0.14
H(26B)…H(40C)	0.001	0.004	-0.0004	0.0003	0.13
H(40C)…H(26B)	0.001	0.004	-0.0004	0.0003	0.13
H(9C)…H(32)	0.001	0.004	-0.0004	0.000	0.12
H(32)…H(9C)	0.001	0.004	-0.0004	0.0003	0.12
Total energy					~34

Co/Ni 1:8					
O…H					
O(5)…H(32)	0.013	0.051	-0.008	0.002	2.58
H(32)…O(5)	0.013	0.051	-0.008	0.002	2.58
O(5)…H(34)	0.004	0.016	-0.002	0.001	0.58
H(34)…O(5)	0.004	0.016	-0.002	0.001	0.58
C…H					
H(31)…C(1)	0.006	0.027	-0.003	0.002	1.04
C(1)…H(31)	0.006	0.027	-0.003	0.002	1.04
C(14)…H(30)	0.004	0.017	-0.002	0.001	0.64
H(30)…C(14)	0.004	0.017	-0.002	0.001	0.64
C(4)…H(12A)	0.004	0.017	-0.002	0.001	0.61
H(12A)…C(4)	0.004	0.017	-0.002	0.001	0.61
H(14B)…C(19)	0.004	0.013	-0.002	0.001	0.47
C(19)…H(14B)	0.004	0.013	-0.002	0.001	0.47
H(8B)…C(14)	0.002	0.009	-0.001	0.001	0.31
C(14)…H(8B)	0.002	0.009	-0.001	0.001	0.31
H(39B)…C(41)	0.001	0.005	-0.001	0.000	0.16
C…C					
C(29)…C(30)	0.005	0.016	-0.002	0.001	0.72
C(30)…C(29)	0.005	0.016	-0.002	0.001	0.72
H…H					
H(34)…H(28B)	0.004	0.019	-0.002	0.001	0.70
H(28B)…H(34)	0.004	0.019	-0.002	0.001	0.70
H(23B)…H(42C)	0.003	0.019	-0.002	0.001	0.64
H(42C)…H(23B)	0.003	0.019	-0.002	0.001	0.64
H(9A)…H(27B)	0.003	0.019	-0.002	0.001	0.62
H(10A)…H(43B)	0.003	0.019	-0.002	0.001	0.62
H(27B)…H(9A)	0.003	0.019	-0.002	0.001	0.62
H(43B)…H(10A)	0.003	0.019	-0.002	0.001	0.62
H(27C)…H(30)	0.004	0.016	-0.002	0.001	0.56
H(30)…H(27C)	0.004	0.016	-0.002	0.001	0.56
H(19)…H(36A)	0.002	0.017	-0.002	0.001	0.51
H(10C)…H(24C)	0.003	0.014	-0.002	0.001	0.50
H(24C)…H(10C)	0.003	0.014	-0.002	0.001	0.50
H(4)…H(13C)	0.003	0.014	-0.002	0.001	0.49
H(13C)…H(4)	0.003	0.014	-0.002	0.001	0.49
H(14A)…H(31)	0.003	0.013	-0.002	0.001	0.48
H(31)…H(14A)	0.003	0.013	-0.002	0.001	0.48
H(26C)…H(41A)	0.003	0.013	-0.001	0.001	0.41
H(41A)…H(26C)	0.003	0.013	-0.001	0.001	0.41
H(5)…H(42A)	0.003	0.011	-0.001	0.001	0.40
H(8B)…H(12C)	0.003	0.011	-0.001	0.001	0.40
H(12C)…H(8B)	0.003	0.011	-0.001	0.001	0.40
H(42A)…H(5)	0.003	0.011	-0.001	0.001	0.40
H(19)…H(40B)	0.002	0.012	-0.001	0.001	0.38
H(40B)…H(19)	0.002	0.012	-0.001	0.001	0.38
H(13B)…H(18)	0.002	0.009	-0.001	0.001	0.32
H(18)…H(13B)	0.002	0.009	-0.001	0.001	0.32
H(24A)…H(26A)	0.002	0.010	-0.001	0.001	0.32
H(26A)…H(24A)	0.002	0.010	-0.001	0.001	0.32
H(23B)…H(35)	0.002	0.010	-0.001	0.001	0.30

H(35)…H(23B)	0.002	0.010	-0.001	0.001	0.30
H(4)…H(43C)	0.002	0.008	-0.001	0.001	0.28
H(27B)…H(29)	0.002	0.009	-0.001	0.001	0.28
H(29)…H(27B)	0.002	0.009	-0.001	0.001	0.28
H(43C)…H(4)	0.002	0.008	-0.001	0.001	0.28
H(24A)…H(28C)	0.002	0.008	-0.001	0.001	0.24
H(28C)…H(24A)	0.002	0.008	-0.001	0.001	0.24
H(9B)…H(26B)	0.001	0.007	-0.001	0.001	0.21
H(26B)…H(9B)	0.001	0.007	-0.001	0.001	0.21
H(28A)…H(36A)	0.002	0.007	-0.001	0.0005	0.21
H(36A)…H(28A)	0.002	0.007	-0.001	0.0005	0.21
H(24B)…H(40A)	0.001	0.007	-0.001	0.001	0.20
H(40A)…H(24B)	0.001	0.007	-0.001	0.001	0.20
H(12C)…H(22B)	0.001	0.005	-0.0005	0.0004	0.15
H(36A)…H(19)	0.002	0.017	-0.002	0.001	0.51
H(26B)…H(40C)	0.001	0.004	-0.0003	0.0003	0.11
H(40C)…H(26B)	0.001	0.004	-0.0003	0.0003	0.11
H(9C)…H(32)	0.001	0.003	-0.0003	0.0002	0.09
H(10B)…H(40C)	0.001	0.003	-0.0003	0.0002	0.09
H(32)…H(9C)	0.001	0.003	-0.0003	0.0002	0.09
H(40C)…H10B)	0.001	0.003	-0.0003	0.0002	0.09
Total energy					33

Table S5. Unit cell parameters for solid solution 1:4 at 240, 200 and 150 K.

Temperature	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	V (Å^3)	$V_{molecule}$ (Å^3)
240	10.7509(2)	15.6732(3)	26.9924(6)	100.866(2)	4466.70(16)	1116.7
200	10.7388(2)	15.6003(2)	26.9877(5)	100.788(2)	4441.30(13)	1110.3
150	10.7123(2)	15.4635(2)	26.9889(5)	100.441(2)	4396.68(13)	1099.2

Table S6. The voids in a unit cell for solid solution 1:4 at 240, 200 and 150 K.

Temperature	Number of voids in a unit cell	Volume of voids, Å^3	Total volume of voids in a unit cell, Å^3
240	12	14 – 51	392
200	12	13 – 49	370
150	12	11 – 45	349

Table S7. Short contacts in crystals of "pure" cobalt and nickel complexes, as well as their solid solutions 1:1, 1:4 and 1:8 at different temperatures.

Number	Atom1	Atom2	Length	Length-VdW	Symm. op. 2
1 (Co), T = 240 K					
1	C34	C28	3.351	-0.049	-1+x,y,z
2	O5	C32	2.897	-0.323	1-x,-1/2+y,1/2-z
3	O5	H32	2.474	-0.246	1-x,-1/2+y,1/2-z
4	C1	H31	2.693	-0.207	1-x,1-y,1-z
1:**1**, T = 240 K					
1	C34	C28	3.363	-0.037	-1+x,y,z
2	O5	C32	2.906	-0.314	1-x,-1/2+y,1/2-z
3	O5	H32	2.444	-0.276	1-x,-1/2+y,1/2-z
4	C1	H31	2.710	-0.190	1-x,1-y,1-z
1:**4**, T = 240 K					
1	C34	C28	3.367	-0.033	-1+x,y,z
2	O5	C32	2.909	-0.311	1-x,-1/2+y,1/2-z
3	O5	H32	2.432	-0.288	1-x,-1/2+y,1/2-z
4	C1	H31	2.722	-0.178	1-x,1-y,1-z
1:**4**, T = 200 K					
1	C34	C28	3.356	-0.044	-1+x,y,z
2	O5	C32	2.905	-0.315	1-x,-1/2+y,1/2-z
3	O5	H32	2.424	-0.296	1-x,-1/2+y,1/2-z
4	C4	H12A	2.893	-0.007	1-x,-y,1-z
5	C1	H31	2.694	-0.206	1-x,1-y,1-z
6	C6	H31	2.887	-0.013	1-x,1-y,1-z
7	C29	C31	3.390	-0.010	1-x,1-y,1-z
1:**4**, T = 150 K					
1	C34	C28	3.341	-0.059	-1+x,y,z
2	O5	C32	2.904	-0.316	1-x,-1/2+y,1/2-z
3	O5	H32	2.422	-0.298	1-x,-1/2+y,1/2-z
4	H23B	H42C	2.388	-0.012	1-x,-1/2+y,1/2-z
5	C4	H12A	2.861	-0.039	1-x,-y,1-z
6	C1	H31	2.670	-0.230	1-x,1-y,1-z
7	C6	H31	2.848	-0.052	1-x,1-y,1-z
8	C29	C31	3.359	-0.041	1-x,1-y,1-z
1:**8**, T = 240 K					

1	C34	C28	3.371	-0.029	-1+x,y,z
2	O5	C32	2.913	-0.307	1-x,-1/2+y,1/2-z
3	O5	H32	2.431	-0.289	1-x,-1/2+y,1/2-z
4	C1	H31	2.731	-0.169	1-x,1-y,1-z
1:**8**, T = 200 K					
1	C34	C28	3.355	-0.045	-1+x,y,z
2	O5	C32	2.911	-0.309	1-x,-1/2+y,1/2-z
3	O5	H32	2.429	-0.291	1-x,-1/2+y,1/2-z
4	C4	H12A	2.899	-0.001	1-x,-y,1-z
5	C1	H31	2.696	-0.204	1-x,1-y,1-z
6	C6	H31	2.888	-0.012	1-x,1-y,1-z
7	C29	C31	3.392	-0.008	1-x,1-y,1-z
1:**8**, T = 130 K					
1	C34	C28	3.343	-0.057	-1+x,y,z
2	O5	C32	2.902	-0.318	1-x,-1/2+y,1/2-z
3	O5	H32	2.422	-0.298	1-x,-1/2+y,1/2-z
4	C4	H12A	2.866	-0.034	1-x,-y,1-z
5	C1	H31	2.675	-0.225	1-x,1-y,1-z
6	C6	H31	2.856	-0.044	1-x,1-y,1-z
7	C29	C30	3.396	-0.004	1-x,1-y,1-z
8	C29	C31	3.376	-0.024	1-x,1-y,1-z
2 (Ni), T = 240 K					
1	C34	C28	3.353	-0.047	-1+x,y,z
2	O5	C32	2.904	-0.316	1-x,-1/2+y,1/2-z
3	O5	H32	2.411	-0.309	1-x,-1/2+y,1/2-z
4	C1	H31	2.712	-0.188	1-x,1-y,1-z
5	C6	H31	2.894	-0.006	1-x,1-y,1-z
6	C29	C31	3.398	-0.002	1-x,1-y,1-z
2 (Ni), T = 100 K					
1	C34	C28	3.320	-0.080	-1+x,y,z
2	O5	C32	2.913	-0.307	1-x,-1/2+y,1/2-z
3	O5	H32	2.434	-0.286	1-x,-1/2+y,1/2-z
4	C4	H12A	2.859	-0.041	1-x,-y,1-z
5	C1	H31	2.659	-0.241	1-x,1-y,1-z
6	C6	H31	2.841	-0.059	1-x,1-y,1-z
7	C29	C30	3.386	-0.014	1-x,1-y,1-z
8	C29	C31	3.354	-0.046	1-x,1-y,1-z

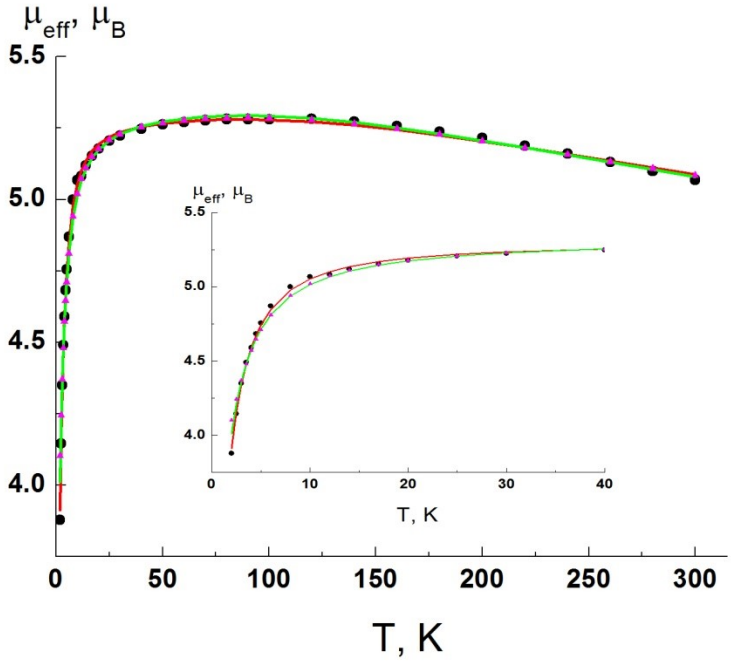

Figure S1. Temperature dependences of the effective magnetic moment for complex **2**. Solid lines are theoretical curves for different models.

Different models may be used for the analysis of the experimental $\mu_{eff}(T)$ dependence for the complex 2. Magenta triangles (▲) correspond to the simplest model with the best fit parameters g_{Ni} = 2.17±0.01, $g_{SQ}=g_{TEMPO}$=2.0 (fixed), $J_{Ni\text{-}SQ}$=154±4 cm^{-1}; $J_{Ni\text{-}NO}$=-1.70±0.03 cm^{-1} (Spin Hamiltonian $H = -2\ J_{Ni\text{-}SQ}\cdot(S_{Ni}S_{SQ1}+S_{Ni}S_{SQ2}) - J_{Ni\text{-}NO}\cdot S_{Ni}S_{NN}$). Red line corresponds to the model with ZFS parameter D taken into account with the best fit parameters g_{Ni} = 2.13±0.01, $g_{SQ} = g_{TEMPO}$ = 2.0 (fixed), $J_{Ni\text{-}SQ}$ = 162±2 cm^{-1}; $J_{Ni\text{-}NO}$ = -1.14±0.06, D = 12.9±1.2 cm^{-1} (Spin Hamiltonian $H = -2\ J_{Ni\text{-}SQ}\cdot(S_{Ni}S_{SQ1}+S_{Ni}S_{SQ2}) - J_{Ni\text{-}NO}\cdot S_{Ni}S_{NN} - D\cdot S_z^2{}_{Ni}$) and green line corresponds to the model with intermolecular exchange interactions zJ' instead of ZFS parameter D for Ni(II) ion. The difference between theoretical curves is small, but models with zero-field splitting parameter D or intermolecular exchange interactions zJ' describe experimental $\mu_{eff}(T)$ dependence slightly better in the low temperature region in comparison with the simplest model. The models are not sensitive to the exchange interactions $J_{SQ\text{-}SQ}$ between semiquinone ligands, and to avoid overparameterization it was fixed at $J_{SQ\text{-}SQ}$ = 0.

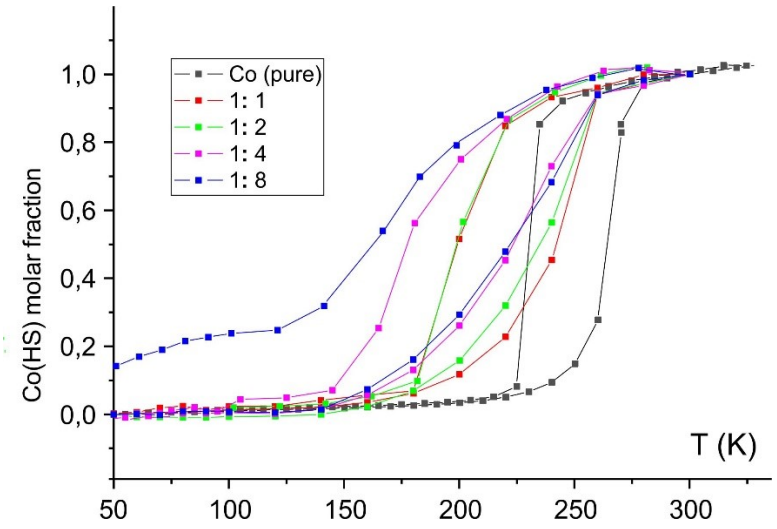

Figure S2. Temperature dependence of the mole fraction of high spin redox isomer.

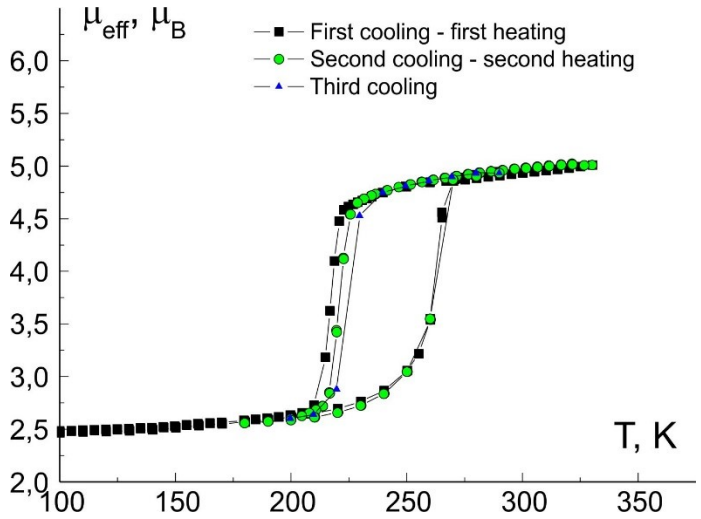

Figure S3. Temperature dependences of the effective magnetic moment for complex **1** during several cooling-heating cycles: 300 K → 2 K → 330 K (–■–); 330 K → 180 K → 290 K (–●–); 290 K → 200 K (–▲–).

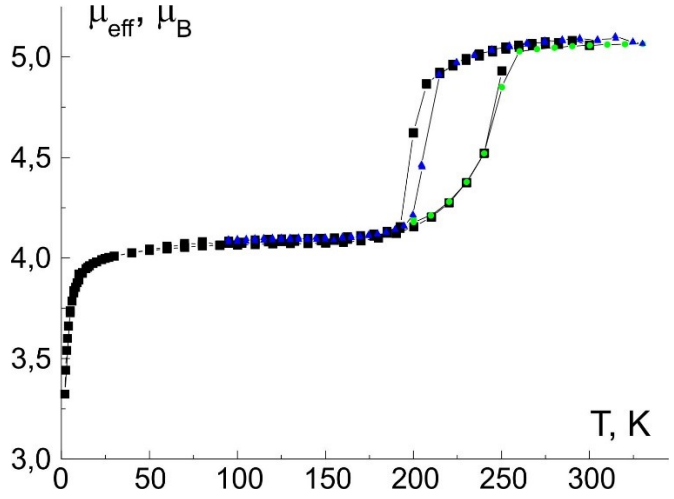

Figure S4. Temperature dependences of the effective magnetic moment for 1:1 solid solution during several cooling-heating cycles: 300 K → 2 K → 250 K (–■–); 200 K → 330 K (–●–) and 330 K → 95 K (–▲–).

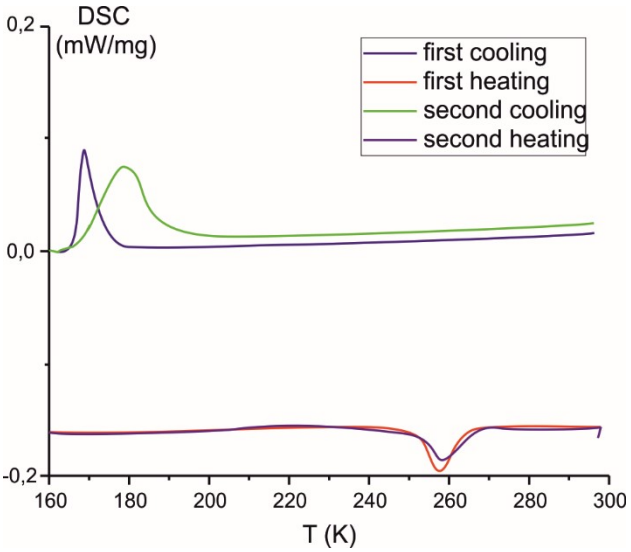

Figure S5. DSC curves for solid solution of 1:2 in the cooling and heating modes.

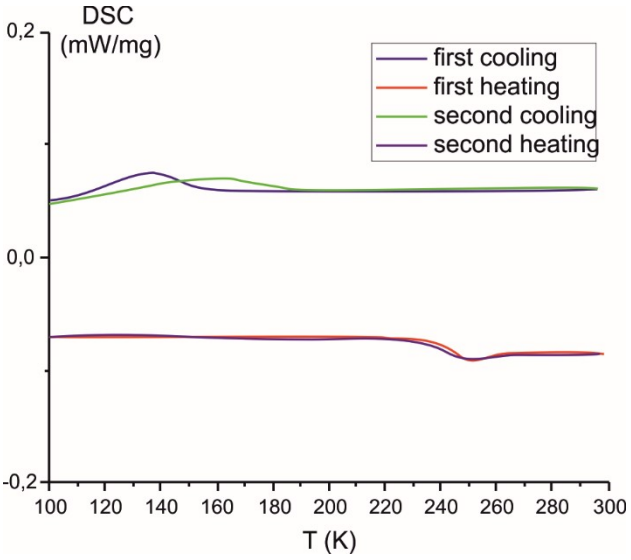

Figure S6. DSC curves for solid solution of 1:4 in the cooling and heating modes.

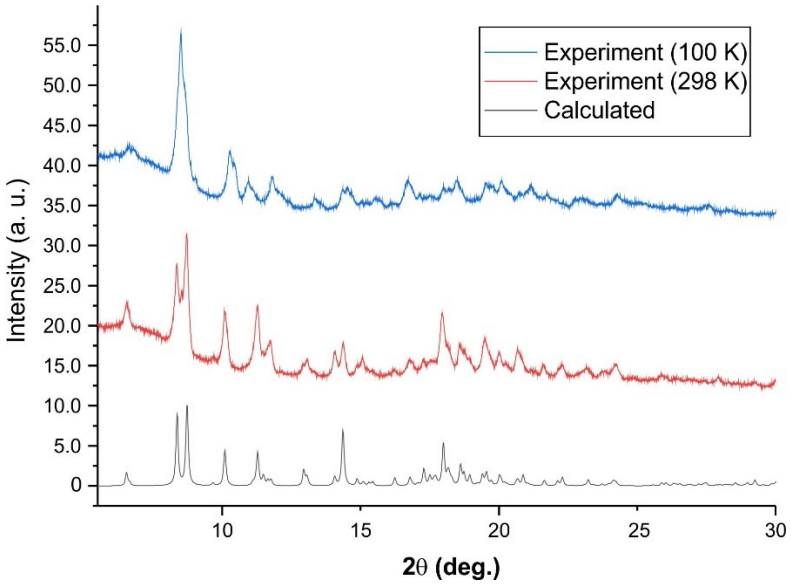

Figure S7. Powder XRD patterns of 1:4 solid solution (experimental at two temperatures and calculated from SC-XRD).

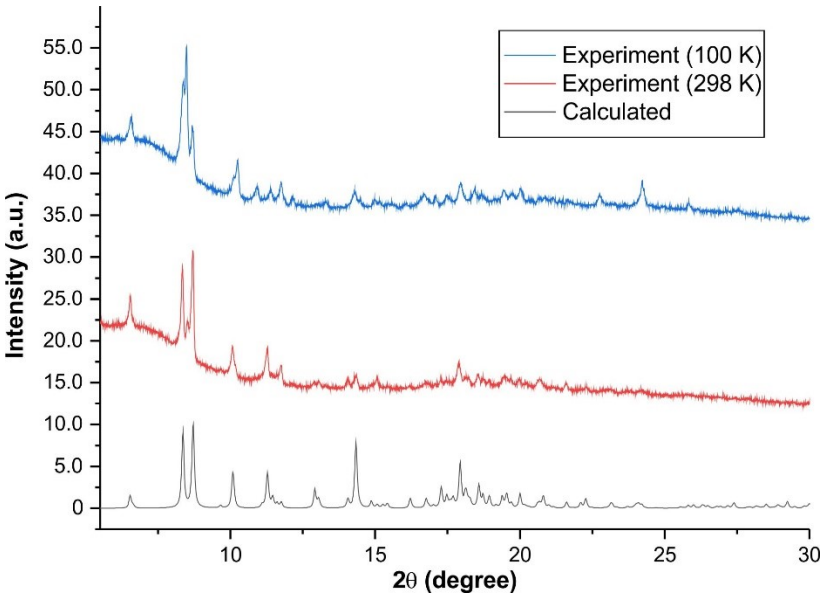

Figure S8. Powder XRD patterns of 1:8 solid solution (experimental at two temperatures and calculated from SC-XRD).

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[*] Alexey A. Zolotukhin, Michael P. Bubnov, Alla V. Arapova, Georgy K. Fukin, Roman V. Rumyantcev, Artem S. Bogomyakov, Alexander V. Knyazev, Vladimir K. Cherkasov, The valence tautomeric interconversion in bis-dioxolene cobalt complex with imino-pyridine functionalized by TEMPO moiety. Phase transition coupled with monocrystals destruction. Inorg. Chem. 2017, 56, 14751−14754.

[**] According to the Espinosa–Molins–Lecomte correlation: Espinosa, E.; Molins, E.; Lecomte, C. Hydrogen bond strengths revealed by topological analyses of experimentally observed electron densities. Chemical Physics Letters, 1998, 285, 170–173.