-Supporting Information-

Influence of the Metal Coordination and the Co-ligand on the Relaxation Properties of 1D Co(NCS)₂ Coordination Polymers

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Figure S1. View of the arrangement of the chains with differently oriented co-ligands in the crystal structures of compounds of the general composition $[Co(NCX)_2(L)_2]_n$ (X = S, Se; L = neutral N-donor co-ligand). For clarity, only the 6-membered rings of the different co-ligands are shown and the hydrogen atoms are omitted.

compound	1	2
formula	$C_{16}H_{14}CoN_4S_2$	$C_{26}H_{18}CoN_4O_2S_2$
MW / g mol ⁻¹	385.36	541.49
crystal system	triclinic	orthorhombic
space group	<i>P</i> -1	$P2_{1}2_{1}2_{1}$
<i>a</i> / Å	9.1050(5)	6.7549(2)
b / Å	10.7073(6)	11.0133(3)
<i>c</i> / Å	11.0049(6)	32.2549(11)
<i>a</i> / °	115.112(4)	90
β / °	93.167(5)	90
γ/\circ	110.952(4)	90
$V/Å^3$	879.62(8)	2399.56(13)
T / K	200	200
Ζ	2	4
$D_{\rm calc}$ / g cm ⁻³	1.455	1.499
μ / mm ⁻¹	1.215	0.921
$\theta_{\rm max}$ / deg	2.11-28.00	1.954-24.595
measured refl.	14007	16688
unique refl.	4232	3998
refl. $[F_0 > 4\sigma(F_0)]$	2851	3751
parameters	247	316
$R_{\rm int}$	0.0353	0.0327
$R_1 [F_0 > 4\sigma(F_0)]$	0.0400	0.0264
wR_2 [all data]	0.0900	0.0626
GOF	1.044	1.053
$\Delta \rho_{\text{max/min}}$ / e Å ⁻³	0.313/-0.430	0.766 / -0.193

Table S1. Selected crystal data and details of the structure refinement for compounds 1 and 2.



Figure S2. IR spectrum of **1**. Given is the value for the CN stretching vibration of the thiocyanato anion.



Figure S3. IR spectrum of **2**. Given is the value for the CN stretching vibration of the thiocyanato anion.



Figure S4. ORTEP plot of **1** with labeling and displacement ellipsoids drawn at 50 % probability level. Symmetry codes: A = -x+2, y+1, -z+1; B = -x+1, -y, -z+1; C = x-1, y-1, z.

Table S2. Selected distances (Å) and angles (°) for 1.

$[Co(NCS)_2(4-vinylpyridine)_2]_n$						
Co(1)–N(2A)	2.0757(19)	Co(2)–N(1B)	2.050(2)			
Co(1)–N(2)	2.0757(19)	Co(2)–N(21)	2.164(2)			
Co(1)–N(11)	2.147(2)	Co(2)–N(21B)	2.164(2)			
Co(1)–N(11A)	2.147(2)	Co(2)–S(2A)	2.6051(7)			
Co(1)-S(1)	2.5862(7)	Co(2)–S(2C)	2.6051(7)			
Co(1)-S(1A)	2.5862(7)					
N(2A)-Co(1)-N(2)	180.00(7)	N(1B)-Co(2)-N(1)	180.00			
N(2A)-Co(1)-N(11)	89.78(8)	N(1B)-Co(2)-N(21)	90.32(8)			
N(2)–Co(1)–N(11)	90.22(8)	N(1)-Co(2)-N(21)	89.68(8)			
N(2A)-Co(1)-N(11A)	90.22(8)	N(1B)-Co(2)-N(21B)	89.68(8)			
N(2)–Co(1)–N(11A)	89.78(8)	N(1)-Co(2)-N(21B)	90.32(8)			
N(11)-Co(1)-N(11A)	180.00	N(21)-Co(2)-N(21B)	180.00			
N(2A)-Co(1)-S(1)	93.86(6)	N(1B)-Co(2)-S(2A)	87.53(6)			
N(2)-Co(1)-S(1)	86.14(6)	N(1)-Co(2)-S(2A)	92.47(6)			
N(11)-Co(1)-S(1)	89.73(6)	N(21)-Co(2)-S(2A)	90.35(6)			
N(11)-Co(1)-S(1)	90.27(6)	N(21B)-Co(2)-S(2A)	89.65(8)			
N(2A)-Co(1)-S(1A)	86.14(6)	N(1B)-Co(2)-S(2C)	92.47(6)			
N(2)-Co(1)-S(1A)	93.86(6)	N(1)-Co(2)-S(2C)	87.53(6)			
N(11)-Co(1)-S(1A)	90.27(6)	N(21)-Co(2)-S(2C)	89.65(8)			
N(11A)-Co(1)-S(1A)	89.73(6)	N(21B)-Co(2)-S(2C)	90.35(6)			
S(1)-Co(1)-S(1A)	180.0	S(2A)-Co(2)-S(2C)	180.00(2)			



Figure S5. ORTEP plot of **2** with labeling and displacement ellipsoids drawn at 50 % probability level. Symmetry codes: A = -x+1, y-1/2, -z+1/2; B = -x+1, y+1/2, -z+1/2.

Table S3. Selected distances (Å) and angles ((°)	for 2 .
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$[Co(NCS)_2(4-benzoylpyridine)_2]_n$					
Co(1)–N(2)	2.073(3)	Co(1)–N(31)	2.177(3)		
Co(1)-N(1)	2.080(3)	Co(1)-S(1A)	2.5576(10)		
Co(1)–N(11)	2.166(3)	Co(1)–S(2B)	2.5769(9)		
N(2)-Co(1)-N(1)	91.04(10)	N(11)-Co(1)-S(1A)	94.18(8)		
N(2)-Co(1)-N(11)	88.43(11)	N(31)-Co(1)-S(1A)	88.38(8)		
N(1)Co(1)-N(11)	89.65(11)	N(2)-Co(1)-S(2B)	173.95(8)		
N(2)-Co(1)-N(31)	89.55(11)	N(1)-Co(1)-S(2B)	94.71(8)		
N(1)-Co(1)-N(31)	87.98(10)	N(11)-Co(1)-S(2B)	89.72(8)		
N(11)-Co(1)-N(31)	176.85(10)	N(31)-Co(1)-S(2B)	92.54(8)		
N(2)-Co(1)-S(1A)	94.43(8)	S(1A)-Co(1)-S(2B)	79.96(3)		
N(1)-Co(1)-S(1A)	173.40(8)		·		



Figure S6. View of the arrangement of the $Co(NCS)_2$ chains in the crystal structure of compound 1 (top) and 2 (bottom).



Figure S7. Experimental (A) and calculated (B) XRPD pattern for 1.



Figure S8. Experimental (A) and calculated (B) XRPD pattern for 2.



Figure S9. ln ($\chi_{mol}T$) vs. reciprocal temperature for **1** and **2**. Experimental data were obtained in field of 100 Oe. The slope of the linear part for **1** is 11.6±0.2 K, and for **2** is 13.6±0.2 K.



Figure S10. DC magnetic susceptibility of **2** measured in various magnetic fields in ZFC/FC mode.



Figure S11. Field dependent magnetization of 2 measured in both field directions in a limited field range ± 1 kOe.



Figure S12. Field dependent magnetization of 2 measured in the field range 0-1000 Oe.



Figure S13. Field dependent magnetization of 1 measured in the field range 0-1000 Oe.



Figure S14. Hysteresis loop measured at 1.8 K for 2 after zero-field cooling in a small field range.

Comment to a small jump of magnetization observed for **2** near H=0 Oe; inset to Fig.6 in the paper.

This jump appears in the same temperature range (below 2.2 K) together with a narrow hysteresis loop, which is seen in Fig.6 as splitting of M(H) curve in the field range 250 – 500 Oe. The width of this loop increases with decreasing temperature. Both, the jump and the loop, seem to be related with the bifurcations mentioned in the paper. That might mean that the metamagnetic transition is not fully reversible, however another small hysteresis loop is also observed for the zero-field cooled sample, when it is registered in a very small field range (±100 Oe), see Figure S12. This loop obtained in fields significantly below H_c may be not directly related to the metamagnetic transition.



Figure S15. Differentiation of the χT curves to obtain critical temperatures.



Figure S16. Specific heat of 2 measured at different magnetic fields.



Figure S17. Specific heat of 1 measured at different magnetic fields.



Figure S18. Specific heat *C* measured for **2** (points) with estimated phonon contribution (dashed green line), and the contribution of exchange interaction (blue solid), and their sum (red).



Figure S19. Specific heat of 1 with analysis (see main text).



Fig. S20. Temperature dependence of χ_{AC} registered at various frequencies for 1 and 2 in field close to H_c . Solid lines are only guides for the eye.



Figure S21. Cole-Cole plots for **1** and **2** obtained for zero field (samples were pressed into pastilles). One solid line for **1** is an exemplary fit.



Figure S22. Cole-Cole plots for **1** and **2** near the critical field (samples were pressed into pastilles). Solid lines are only guides for the eye.

<i>T</i> (K)	χ_{∞} (emu/mol)	$\chi_{0-\chi_{\infty}}$ (emu/mol)	$\tau_{1}(s)$	α_1	$\chi_{ m sq}^2$
1.8	0.078	0.752	9.17·10 ⁻³	0.54	1.25.10-5
1.9	0.063	0.787	3.99.10-3	0.54	2.26.10-5
2.0	0.040	0.88	1.66.10-3	0.54	2.86.10-5
2.1	0.004	0.884	6.54·10 ⁻⁴	0.54	3.31.10-5
2.3	0.0	0.91	1.61.10-4	0.49	3.38.10-5
2.4	0.0	0.93	7.49.10-5	0.46	2.62.10-5
2.5	0.0	0.96	3.746.10-5	0.42	1.80.10-5
2.6	0.0	1.0	1.929.10-5	0.38	9.46.10-6
2.7	0.0	1.06	1.203.10-5	0.30	5.65.10-6
2.8	0.0	1.15	8.010.10-6	0.21	3.97.10-6

Table S4. Fitting results of the frequency dependencies for $1 (H_{DC} = 5 \text{ Oe})$.

Table S5. Fitting results of the frequency dependencies for $2 (H_{DC} = 5 \text{ Oe})$.

<i>T</i> (K)	χ_{∞} (emu/mol)	$\chi_{0-\chi_{\infty}}$ (emu/mol)	$\tau(s)$	α	$\chi_{ m sq}^2$
1.8	0.042	0.607	6.82·10 ⁻²	0.58	4.11.10-5
1.9	0.0513	0.58	$2.98 \cdot 10^{-2}$	0.54	1.09.10-5
2.0	0.044	0.581	$1.24 \cdot 10^{-2}$	0.52	1.54.10-5
2.1	0.041	0.576	5.05.10-3	0.51	6.50.10-6
2.17	0.041	0.572	2.93.10-3	0.50	1.10.10-5
2.3	0.047	0.561	1.03.10-3	0.47	6.49.10-6
2.4	2.4 0.0347	0.575	3.68.10-4	0.45	1.33.10-6
2.5	0.030	0.587	1.38.10-4	0.42	1.68.10-6
2.6	0.0	0.636	5.21.10-5	0.37	3.61.10-6
2.7	0.0	0.677	$2.75 \cdot 10^{-5}$	0.26	1.13.10-5
2.8	0.20	0.551	2.20.10-5	0.17	5.13.10-6
2.9	0.123	0.769	8.57.10-6	0.16	7.35.10-6



Figure S23. CDFT and BSDFT computational models for **1** (left) and **2** (right). The pink spheres designate Na(I) ions to compensate the charges of the dianionic fragments.

	Compound	State	2 <i>S</i> +1	$E_{\rm rel}$ / a.u.	$\langle S^2 \rangle$	Equation	J/K
				CDF	T		
	1	HS	7	-7339.019299	12.020	(1)	27.6
	1	BS	1	-7339.017727	3.020	(1)	27.0
	ſ	HS	7	-8406.162996	12.022	(1)	25.2
	2	BS	1	-8406.160983	3.020	(1)	33.3
				BSD	FT		
	1	HS	7	-7337.236689	12.019	(2)	100 (
	1	BS	1	-7337.235127	3.017	(2)	109.6
	2	HS	7	-8403.792290	12.019	(2)	17
2	2	BS	1	-8403.792357	3.017	(2)	-4./

 Table S6. Results of CDFT and BSDFT calculations for 1 and 2.



Figure S24. CDFT spin densities of **1** for high-spin (first row) and broken-symmetry (second row) states. Red (cyan) isosurfaces represent net α (β) spin densities (iso-value 0.002). The two pictures on the right show a view from the top without the 4-vinylpyridine ligands.



Figure S25. CDFT spin densities of **2** for high-spin (first row) and broken-symmetry (second row) states. Red (cyan) isosurfaces represent net α (β) spin densities (iso-value 0.002). The two pictures on the right show a view from the top without the 4-benzoylpyridine ligands.

Figure S26. *Ab initio* computational models for **1-Co1** (left), **1-Co2** (center), and **2** (right). The pink spheres designate Na(I) ions to compensate the charges of the dianionic fragments.

1-Co		C 01	1-(C o2	2	
23+1	CASSCF	CASPT2	CASSCF	CASPT2	CASSCF	CASPT2
4	0	0	0	0	0	0
	619	1312	464	491	109	80
	660	1004	520	1385	332	1281
	5597	6828	5344	6592	6785	7574
	7964	9252	7621	8874	6913	7721
	8494	9475	8626	9627	7437	8839
	15625	17776	15493	17664	15080	17247
	22007	18142	21647	21795	21759	17872
	22226	22409	22134	18325	22936	22602
	25645	25479	25876	25743	23390	23081
2	12018	9173	11705	9030	13085	9791
	15480	13321	15672	13456	14088	12620
	18098	16148	17533	15760	19261	16882
	18554	16409	18420	16400	19277	16874
	19305	17122	19086	16962	19336	16948
	20022	17879	20051	17885	19751	18914
	20340	19117	20315	18974	20010	18252
	21290	19123	21181	19016	20102	18303
	24561	21550	24189	19482	24749	23874
	24612	22134	24481	21031	24878	21793
	24812	23849	24622	23652	24936	22076
	25179	22693	24936	22838	25184	22222

Table S7. Relative CASSCF and CASPT2 energies (in cm^{-1}) of all quartet and the 12 lowest doublet states for 1 and 2.

Table S8. Relative RASSI-SO energies (cm⁻¹) for 1 and 2.

Kramers doublet	1-Co1	1-Co2	2
1	0	0	0
2	183	192	270
3	802	718	515
4	1011	941	812
5	2023	1760	1825
6	2068	1810	1861

Figure S27. *Ab initio* calculated ($S_{eff} = 1/2$) magnetic axes (blue dashed lines: easy-axes; red dashed lines: hard-axes) for the ground state KD of **1-Co1**, **1-Co2**, and **2** projected onto dinuclear Co(II) fragments of **1** (left and center left) and **2** (center right and right). The angle between the two easy-axes of **1-Co1** and **1-Co2** is 9.1°. Hydrogen atoms as well as pyridine-based co-ligands in top views (center left and right) are omitted for clarity.

Figure S28. *Ab initio* calculated ($S_{eff} = 1/2$) magnetic axes (blue dashed lines: easy-axes; red dashed lines: hard-axes) for the first excited KD state of **1-Co1**, **1-Co2**, and **2** projected onto dinuclear Co(II) fragments of **1** (left and center left) and **2** (center right and right). The angle between the two easy-axes of **1-Co1** and **1-Co2** is 68.1°. Hydrogen atoms as well as pyridine-based co-ligands in top views (center left and right) are omitted for clarity.

Figure S29. Magnetization blocking barriers in **1-Co1** (left) and **1-Co2** (right). Arrows represent the transition between different magnetic states and corresponding values show the average dipole matrix element $\bar{\mu}_z$ in respect to the ground state easy-axis orientation.

Figure S30. Magnetization blocking barriers in **2**. Arrows represent the transition between different magnetic states and corresponding values show the average dipole matrix element $\bar{\mu}_z$ in respect to the ground state easy-axis orientation.