- Supporting Information -

Variation of the Chain Geometry in Isomeric 1D Co(NCS)₂ Coordination Polymers and Their Influence on the Magnetic Properties

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Figure S1. IR spectrum of **1**. Given are the values for the CN stretching vibrations of the thiocyanato ligand.



Figure S2. IR spectrum of **2**. Given are the values for the CN stretching vibrations of the thiocyanato ligand.



Figure S3. IR spectrum of **3C**. Given are the values for the CN stretching vibrations of the thiocyanato ligand.



Figure S4. IR spectrum of **3L**. Given are the values for the CN stretching vibrations of the thiocyanato ligand.

compound	1	2	3C	3L
Formula	$C_{22}H_{16}Cl_4CoN_6S_2$	$C_{12}H_{12}CI_2CoN_4O_2S_2$	$C_{12}H_8CI_2CoN_4S_2$	$C_{12}H_8CI_2CoN_4S_2$
MW / g mol⁻¹	629.26	438.21	402.17	402.17
crystal system	Trigonal	Monoclinic	Monoclinic	Triclinic
space group	RĪ	P21/c	C2/c	$P\overline{1}$
a / Å	26.1440(8)	10.4167(4)	20.3687(11)	8.0830(5)
b/Å	26.1440(8)	12.1079(4)	8.8343(5)	9.3935(6)
<i>c</i> / Å	11.2720(4)	7.5528(3)	18.9769(9)	10.7022(7)
α/°	90	90	90	73.445(5)
β/°	90	108.135(3)	115.790(5)	83.196(5)
γl°	120	90	90	80.791(5)
V / Å ³	6672.3(5)	905.27(6)	3074.6(3)	766.59(8)
<i>Т </i> К	170(2)	170(2)	200(2)	290(2)
Ζ	9	2	8	2
$D_{\rm calc}$ / g cm ⁻³	1.409	1.608	1.738	1.742
μ / mm⁻¹	1.102	1.484	1.731	1.735
$ heta_{ extsf{max}}$ / deg	26.002	25.749	27.095	28.01
measured refl.	13400	11310	14917	11964
unique refl.	2924	1734	3397	3704
refl. [<i>l</i> > 2 <i>o</i> (<i>l</i>)]	2431	1620	2660	2672
parameter	160	106	193	193
R _{int}	0.0299	0.0299	0.0567	0.0667
$R_1\left[l>2\sigma(l)\right]$	0.0436	0.0197	0.0391	0.0604
wR ₂ [all data]	0.1020	0.0504	0.0947	0.0975
GOF	1.060	1.095	1.024	1.168
$\varDelta ho_{max/min}$ / e Å ⁻³	0.463/ -0.451	0.270/-0.211	0.398/ -0.487	0.519/ -0.423

Table S1. Selected crystal parameters and details of the structure refinements for 1, 2, 3C, and 3L



Figure S5. Crystal structure of compound **1** with labeling and displacement ellipsoids drawn at the 50% probability level. Symmetry code: A = -x+1, -y, -z.

Co(NCS) ₂ (4-chloropyridine) ₄						
Co1–N1A	2.054(2)	Co1–N11A	2.185(2)			
Co1-N1	2.054(2)	Co1–N21A	2.229(2)			
Co1-N11	2.185(2)	Co1-N21	2.229(2)			
N1A-Co1-N1	180.0(3)	N11–Co1–N21A	86.57(9)			
N1A-Co1-N11	89.81(9)	N11A–Co1–N21A	93.43(9)			
N1-Co1-N11	90.19(9)	N1A–Co1–N21	90.69(10)			
N1A–Co1–N11A	90.19(9)	N1–Co1–N21	89.31(10)			
N1–Co1–N11A	89.81(9)	N11–Co1–N21	93.43(9)			
N11-Co1-N11A	180.0	N11A–Co1–N21	86.57(9)			
N1A–Co1–N21A	89.32(10)	N21A–Co1–N21	180.0			
N1-Co1-N21A	90.68(10)	N11-Co1-N21A	86.57(9)			

Table S2. Selected bond lengths (in Å) and angles (in °) for ${\bf 1}$



Figure S6. Crystal structure of compound **2** with labeling and displacement ellipsoids drawn at the 50% probability level. Symmetry code: A = -x+1, -y+1, -z+1.

Co(NCS) ₂ (4-chloropyridine) ₂ (H ₂ O) ₂						
Co1-N1	2.0798(13)	Co1-01A	2.0863(10)			
Co1–N1A	2.0798(13)	Co1-N11	2.1677(12)			
Co1-01	2.0863(10)	Co1–N11A	2.1677(12)			
N1–Co1–N1A	180.0	O1A–Co1–N11	91.50(5)			
N1-Co1-O1	92.42(5)	N1–Co1–N11A	89.99(5)			
N1A-Co1-O1	87.58(5)	N1A–Co1–N11A	90.01(5)			
N1-Co1-O1A	87.58(5)	01–Co1–N11A	91.50(5)			
N1A-Co1-O1A	92.42(5)	O1A–Co1–N11A	88.50(5)			
01–Co1–O1A	180.00(6)	N11–Co1–N11A	180.0			
N1-Co1-N11	90.01(5)	C1–N1–Co1	158.66(12)			
N1A-Co1-N11	89.99(5)	C15-N11-Co1	122.03(10)			
01-Co1-N11	88.50(5)	C11-N11-Co1	120.83(10)			

Table S3. Selected	bond lengths	(in Å) and	angles (ir	ի °) for 2



Figure S7. Part of the crystal structure of compound **2** with view along the *a*-axis onto a layer formed by intermolecular hydrogen bonding, which is shown as dashed lines.



Figure S8. Crystal structure of compound **3C** with labeling and displacement ellipsoids drawn at the 50% probability level. Symmetry code: A = -x, y, -z+1/2, B = -x+1/2, -y+1/2, -z+1.



Figure S9. Crystal structure of compound **3L** with labeling and displacement ellipsoids drawn at the 50% probability level. Symmetry code: A = -x+1, -y+1, -z+1, B = -x+2, -y, -z+1.

	Co(NCS) ₂ (4-chl	oropyridine) ₂ (3C)	
Co1-N2A	2.062(2)	Co2-N1	2.054(2)
Co1-N2	2.062(2)	Co2-N1B	2.054(2)
Co1-N11	2.170(2)	Co2-N21	2.205(2)
Co1-N11A	2.170(2)	Co2-N21B	2.205(2)
Co1-S1A	2.6010(8)	Co2-S2	2.5628(7)
Co1-S1	2.6010(8)	Co2-S2B	2.5628(7)
N2A-Co1-N2	177.59(14)	N1-Co2-N1B	180.00(13)
N2A-Co1-N11	92.02(9)	N1-Co2-N21	90.81(9)
N2-Co1-N11	89.70(9)	N1B-Co2-N21	89.19(9)
N2A-Co1-N11A	89.70(9)	N1-Co2-N21B	89.19(9)
N2-Co1-N11A	92.02(9)	N1B-Co2-N21B	90.81(9)
N11-Co1-N11A	88.67(12)	N21-Co2-N21B	180.0
N2A-Co1-S1A	93.82(7)	N1-Co2-S2	93.96(7)
N2-Co1-S1A	84.50(7)	N1B-Co2-S2	86.04(7)
N11-Co1-S1A	174.03(6)	N21-Co2-S2	90.29(6)
N11A-Co1-S1A	90.12(6)	N21B-Co2-S2	89.71(6)
N2A-Co1-S1	84.50(7)	N1-Co2-S2B	86.04(7)
N2-Co1-S1	93.82(7)	N1B-Co2-S2B	93.96(7)
N11-Co1-S1	90.12(6)	N21-Co2-S2B	89.71(6)
N11A-Co1-S1	174.03(6)	N21B-Co2-S2B	90.29(6)
S1A-Co1-S1	91.68(4)	S2-Co2-S2B	180.0
	Co(NCS)2(4-chl	oropyridine) ₂ (3L)	
Co1-N1A	2.051(3)	Co2-N2B	2.075(3)
Co1-N1	2.051(3)	Co2-N2	2.075(3)
Co1-N11A	2.171(3)	Co2-N21B	2.160(3)
Co1-N11	2.171(3)	Co2-N21	2.160(3)
Co1-S2	2.6254(11)	Co2-S1	2.5918(11)
Co1-S2A	2.6254(11)	Co2-S1B	2.5918(11)
N1A-Co1-N1	180.0	N2B-Co2-N2	180.0
N1A-Co1-N11A	89.42(13)	N2B-Co2-N21B	88.70(13)
N1-Co1-N11A	90.59(13)	N2-Co2-N21B	91.30(13)
N1A-Co1-N11	90.58(13)	N2B-Co2-N21	91.30(13)
N1-Co1-N11	89.42(13)	N2-Co2-N21	88.70(13)
N11A-Co1-N11	180.0	N21B-Co2-N21	180.00(17)
N1A-Co1-S2	88.00(10)	N2B-Co2-S1	86.21(10)
N1-Co1-S2	92.00(10)	N2-Co2-S1	93.79(10)
N11A-Co1-S2	89.67(9)	N21B-Co2-S1	90.21(10)
N11-Co1-S2	90.33(9)	N21-Co2-S1	89.79(10)
N1A-Co1-S2A	92.00(10)	N2B-Co2-S1B	93.79(10)
N1-Co1-S2A	88.00(10)	N2-Co2-S1B	86.21(10)
N11A-Co1-S2A	90.33(9)	N21B-Co2-S1B	89.79(10)
N11-Co1-S2A	89.67(9)	N21-Co2-S1B	90.21(10)
	100.0	61 Col 61D	190.0

Table S4. Selected bond lengths (in Å) and angles (in °) for 3C and 3L



Figure S10. Arrangement of the chains in the crystal structure of 3C (top) and 3L (bottom).



Figure S11. Experimental (A) and calculated (B) XRPD pattern of 3C.



Figure S12. Experimental (A) and calculated (B) XRPD pattern of 3L obtained from solution.



Figure S13. Experimental (A) and calculated (B) XRPD pattern of **1** obtained from solution. Please note, that the pattern is affected by strong texture.



Figure S14. Experimental (A) and calculated (B) XRPD pattern of 2.



Figure S15. DTA, TG, and DTG curves as well as heating rate dependent measurements for 1.



Figure S16. Experimental XRPD pattern of the residue obtained by thermogravimetric measurements of **1** (A) and **2** (B) together with the calculated pattern of **3L** (C).



Figure S17. DTA, TG, and DTG curves with a heating rate of 1 °C/min (left) as well as heating rate dependent measurements for **2** (right).



Figure S18. Experimental XRPD pattern of the residue obtained by annealing of **2** (A) and calculated XRPD pattern of **3L** (B).



Figure S19. Calculated XRPD pattern of **3L** (A) and **3C** (C) together with the experimental pattern of a mixture of both isomers (B) and after stirring this mixture in methanol for five days (D).



Figure S20. Calculated XRPD pattern of **3L** (A) and **3C** (C) together with the experimental pattern of a mixture of both isomers (B) and after stirring this mixture in ethanol for five days (D).



Figure S21. DSC curve of 3C (top) and 3L (bottom) at 10 °C/min.



Figure S22. Temperature dependent XRPD measurements of 3C.



Figure S23. Temperature dependent XRPD measurements of compound 2.



Figure S24. Temperature dependence of the specific heat *C*, measured for **3C** and **3L** and shown as C/T. Solid lines are fitted as a sum of lattice and spin contributions. The lattice contributions are marked with dashed lines, while the sum is marked with solid lines.



Figure S25. Magnetization of **3C** (triangles) and **3L** (dots) measured at 1.8 K. Inset: Low field magnetization of **3L** at different temperatures from 1.8 to 3 K, showing the metamagnetic transition. Lines are to guide the eye.



Figure S26. The derivative of low-field susceptibility, as used to determine the critical temperature of the antiferromagnetic phase of **3L**.



Figure S27. Ac magnetic susceptibility measured for **3L** at 2 K and different applied dc fields (values given in Oe), shown in Argand plot. The solid lines are fitted using a single mode Cole-Cole model.



Figure S28. Dinuclear structural models $[Co_2Zn_2(NCS)_6(4\text{-chloropyridine})_4]^{2+}$ used in the BS-DFT calculations for **3C** (**3C**-Co1Co2; left) and **3L** (**3L**-Co1Co2; right). The pink spheres designate zinc(II) ions to compensate the negative charge of the structural models.

Computational model	State	2S + 1	E _{rel} (Hartree)	$\langle \hat{S}^2 \rangle$	<i>∆E</i> (cm ⁻¹)	J _{BS} (cm ⁻¹)
3C -Co1Co2	HS	7	-12098.445033	12.050	24.4	4.1
	BS	1	-12098.444922	3.048		
3L -Co1Co2	HS	7	-12098.439272	12.066	18.4	3.1
	BS	1	-12098.439187	3.059		

Table S5. BS-DFT results for the Heisenberg coupling constants (J_{BS})



Figure S29. Spin densities obtained from BS-DFT (iso-value 0.005) for **3C** (first row) and **3L** (second row) for the high-spin state (HS; left column) and broken-symmetry state (BS; right column). Red (cyan) isosurfaces represent net α (β) spin densities.



Figure S30. Overlay of the $[Co_2(NCS)_2]^{2+}$ cores as found in **3C** (red) and **3L** (blue) from two different perspectives. The (NCS)₂ bridges mediate the magnetic exchange between the cobalt(II) ions.



Figure S31. Mononuclear structural models $[CoZn_2(NCS)_4(4-chloropyridine)_2]^{2+}$ for **3C** (first row) and **3L** (second row), used in the *ab initio* calculations. The additional zinc(II) ions attached to compensate the negative charge of the structural models are marked as pink spheres.

25 + 1	Term	Subterm	3C -Co1	3C -Co2	3L -Co1	3L -Co2
4	⁴ F	${}^{4}T_{1g}$	0	0	0	0
			604	408	551	696
			629	997	989	1108
		${}^{4}T_{2g}$	6622	5785	5402	5692
			6631	7308	7709	7897
			8687	8775	8677	8487
		⁴ A ₂	15369	15418	15461	15446
	⁴ P	${}^{4}T_{1g}$	22259	21747	21538	21392
			23281	22321	22238	22774
			23372	25497	26402	25896
2	² G + ² P		13046	12341	11834	12260
			14562	15467	16173	15922
			18593	17982	17564	18188
			19491	19228	18429	18694
			19751	19299	19121	19358
			19778	19770	20156	20078
			20629	20662	20820	20845
			20656	21250	21289	21374
			24805	24627	24342	24444
			25045	24697	24393	24840
			25154	24767	24697	24864
			25251	25132	25068	25220

Table S6. Relative CASSCF energies (in cm^{-1}) of all quartet and the 12 lowest doublet states for the crystallographically independent cobalt(II) centers in **3C** and **3L**

25 + 1	Term	Subterm	3C -Co1	3C -Co2	3L -Co1	3L -Co2
4	⁴ F	${}^{4}T_{1g}$	0	0	0	0
			841	506	580	708
			838	946	823	982
		${}^{4}T_{2g}$	7320	6894	6359	6699
			7346	8444	8702	8978
			9998	9942	9672	9499
		⁴ A ₂	17640	17636	17566	17548
	⁴ P	${}^{4}T_{1g}$	20104	19287	19039	18853
			20628	20137	20011	20604
			20714	23257	24219	23628
2	² G + ² P		10566	9727	9139	9578
			11802	12652	13420	13116
			16773	16059	15545	16064
			16858	16917	16297	16593
			17307	16681	16510	16732
			17351	17048	17427	17322
			17925	17975	18101	18138
			17945	18415	18427	18482
			23273	21198	20674	20882
			21425	22659	21041	22500
			21676	22008	22980	22343
			21677	21365	21235	21352

Table S7. Relative CASPT2 energies (in cm⁻¹) of all quartet and the 12 lowest doublet states for the crystallographically independent cobalt(II) centers in **3C** and **3L**

Table S8. Relative RASSI-SO energies (in cm⁻¹) of the six lowest Kramers doublets of the ${}^{4}T_{1g}$ ground multiplet for the crystallographically independent cobalt(II) centers in **3C** and **3L**

Term	Subterm	KD	3C -Co1	3C -Co2	3L -Co1	3L -Co2
⁴ F	${}^{4}T_{1g}$	1	0	0	0	0
		2	155	174	172	151
		3	764	635	749	801
		4	1090	907	1008	1056
		5	1249	1325	1252	1346
		6	1387	1437	1359	1457



Figure S32. Representation of the magnetic axes for the ground state Kramers doublet ($S_{eff} = 1/2$; color code: red – hard axis of magnetization; green – easy axis of magnetization) as obtained from *ab initio* calculations for the mononuclear model structures of **3C** (first row) and **3L** (second row).



Figure S33. Overlay of the mononuclear cobalt(II) structural models 3C-Co2 (red) and 3L-Co1 (blue).



Scheme S1. Graphical definition of 12-membered spin rings of the type $[\dots A \dots B \dots C \dots D \dots]_3$ to simulate hypothetical chains to investigate the influence on the magnetic properties in **3C**.



Figure S34. Representation of spin states as obtained by the POLY_ANISO program employing the data from *ab initio* calculations for the structural models of **3L** and **3C** (black). For all simulations a 12-membered spin ring coupling scheme together with a positive coupling constant for the Lines model $(J_{ij} > 0)$ were used. For the sake of comparison, the resulting energy range for all cases has been scaled to 6*J* where *J* represents the Ising model coupling constant. The spin states depicted in blue describe the expected multiplet splitting for an ideal Ising anisotropy. Spin states shown in gray represent corresponding calculations based on only one crystallographically independent spin center (**3C**-Co1 and **3C**-Co2). The simulations denoted as **3C**-Co1/C2 and **3C**-Co2/C2 take additionally care of the C_2 symmetry of the compound (for graphical representation see Scheme S1).