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

| compound | 1 | 2 | 3 C | 3L |
| :---: | :---: | :---: | :---: | :---: |
| Formula | $\mathrm{C}_{22} \mathrm{H}_{16} \mathrm{Cl}_{4} \mathrm{CoN}_{6} \mathrm{~S}_{2}$ | $\mathrm{C}_{12} \mathrm{H}_{12} \mathrm{Cl}_{2} \mathrm{CoN}_{4} \mathrm{O}_{2} \mathrm{~S}_{2}$ | $\mathrm{C}_{12} \mathrm{H}_{8} \mathrm{Cl}_{2} \mathrm{CoN}_{4} \mathrm{~S}_{2}$ | $\mathrm{C}_{12} \mathrm{H}_{8} \mathrm{Cl}_{2} \mathrm{CoN}_{4} \mathrm{~S}_{2}$ |
| MW / g mol ${ }^{-1}$ | 629.26 | 438.21 | 402.17 | 402.17 |
| crystal system | Trigonal | Monoclinic | Monoclinic | Triclinic |
| space group | $R \overline{3}$ | $P 2_{1} / \mathrm{c}$ | C2/c | $P \overline{1}$ |
| $a / \AA$ | 26.1440(8) | 10.4167(4) | 20.3687(11) | 8.0830(5) |
| b/A | 26.1440(8) | 12.1079(4) | 8.8343(5) | 9.3935(6) |
| c / A | 11.2720(4) | 7.5528(3) | 18.9769(9) | 10.7022(7) |
| $\alpha /{ }^{\circ}$ | 90 | 90 | 90 | 73.445(5) |
| $\beta /^{\circ}$ | 90 | 108.135(3) | 115.790(5) | 83.196(5) |
| $\gamma 1^{\circ}$ | 120 | 90 | 90 | 80.791(5) |
| $V / \AA^{3}$ | 6672.3(5) | 905.27(6) | 3074.6(3) | 766.59(8) |
| T/K | 170(2) | 170(2) | 200(2) | 290(2) |
| $Z$ | 9 | 2 | 8 | 2 |
| $D_{\text {calc }} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.409 | 1.608 | 1.738 | 1.742 |
| $\mu / \mathrm{mm}^{-1}$ | 1.102 | 1.484 | 1.731 | 1.735 |
| $\theta_{\text {max }} / \mathrm{deg}$ | 26.002 | 25.749 | 27.095 | 28.01 |
| measured refl. | 13400 | 11310 | 14917 | 11964 |
| unique refl. | 2924 | 1734 | 3397 | 3704 |
| refl. [ $/>2 \sigma(I)]$ | 2431 | 1620 | 2660 | 2672 |
| parameter | 160 | 106 | 193 | 193 |
| $R_{\text {int }}$ | 0.0299 | 0.0299 | 0.0567 | 0.0667 |
| $R_{1}[I>2 \sigma(I)]$ | 0.0436 | 0.0197 | 0.0391 | 0.0604 |
| $w R_{2}$ [all data] | 0.1020 | 0.0504 | 0.0947 | 0.0975 |
| GOF | 1.060 | 1.095 | 1.024 | 1.168 |
| $\Delta \rho_{\text {max } / \text { min }} /$ e $\AA^{-3}$ | 0.463/-0.451 | 0.270/-0.211 | 0.398/-0.487 | 0.519/-0.423 |



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

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

|  | $\mathrm{Co}(\mathrm{NCS})_{2}(\text { 4-chloropyridine })_{4}$ |  |  |
| :--- | :--- | :--- | :--- |
| 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 | $86.57(9)$ |



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

Table S3. Selected bond lengths (in Å) and angles (in ${ }^{\circ}$ ) for $\mathbf{2}$

|  | $\mathrm{Co}(\mathrm{NCS})_{2}(4 \text {-chloropyridine })_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}$ |  |  |
| :--- | :--- | :--- | :--- |
| Co1-N1 | $2.0798(13)$ | Co1-O1A | $2.0863(10)$ |
| Co1-N1A | $2.0798(13)$ | Co1-N11 | $2.1677(12)$ |
| Co1-O1 | $2.0863(10)$ | 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 | $87.58(5)$ | O1-Co1-N11A | $91.50(5)$ |
| N1A-Co1-O1A | $92.42(5)$ | O1A-Co1-N11A | $88.50(5)$ |
| O1-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 | $122.03(10)$ |
| O1-Co1-N11 | $88.50(5)$ | C11-N11-Co1 | $120.83(10)$ |



Figure S7. Part of the crystal structure of compound $\mathbf{2}$ 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: $A=-x+1,-y+1,-z+1, B=-x+2,-y,-z+1$.

Table S4. Selected bond lengths (in Å) and angles (in ${ }^{\circ}$ ) for 3C and 3L

| $\mathrm{Co}(\mathrm{NCS})_{2}\left(4\right.$-chloropyridine) ${ }_{2}(3 \mathrm{C})$ |  |  |  |
| :---: | :---: | :---: | :---: |
| 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 |
| $\mathrm{Co}(\mathrm{NCS})_{2}\left(4\right.$-chloropyridine) ${ }_{2}(3 \mathrm{~L})$ |  |  |  |
| 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) |
| S2-Co1-S2A | 180.0 | S1-Co2-S1B | 180.0 |



Figure S10. Arrangement of the chains in the crystal structure of $\mathbf{3 C}$ (top) and $\mathbf{3 L}$ (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 $\mathbf{1}$.


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


Figure S17. DTA, TG, and DTG curves with a heating rate of $1^{\circ} \mathrm{C} / \mathrm{min}$ (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 $10^{\circ} \mathrm{C} / \mathrm{min}$.


Figure S22. Temperature dependent XRPD measurements of 3C.


Figure S23. Temperature dependent XRPD measurements of compound $\mathbf{2}$.


Figure S24. Temperature dependence of the specific heat $C$, measured for 3 C and $\mathbf{3 L}$ 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 3 L 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 $\mathbf{3 L}$.


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.


3C-Co1Co2


3L-Co1Co2

Figure S28. Dinuclear structural models $\left[\mathrm{Co}_{2} \mathrm{Zn}_{2}(\mathrm{NCS})_{6}(4 \text {-chloropyridine })_{4}\right]^{2+}$ 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.

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

| Computational model | State | $2 S+1$ | $E_{\text {rel }}$ (Hartree) | $\left\langle\hat{\mathrm{S}}^{2}\right\rangle$ | $\Delta E\left(\mathrm{~cm}^{-1}\right)$ | $J_{\mathrm{BS}}\left(\mathrm{cm}^{-1}\right)$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 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 |  |  |



3C-Co1Co2 (HS)


3L-Co1Co2 (HS)


3C-Co1Co2 (BS)


3L-Co1Co2 (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 $\alpha(\beta)$ spin densities.


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


3C-Co1




Figure S31. Mononuclear structural models $\left[\mathrm{CoZn}_{2}(\mathrm{NCS})_{4}(4 \text {-chloropyridine) })_{2}\right]^{2+}$ for 3 C (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.

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

| $2 S+1$ | Term | Subterm | 3C-Co1 | 3C-Co2 | 3L-Co1 | 3L-Co2 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 4 | ${ }^{4} \mathrm{~F}$ | ${ }^{4} \mathrm{~T}_{1 \mathrm{~g}}$ | 0 | 0 | 0 | 0 |
|  |  |  | 604 | 408 | 551 | 696 |
|  |  |  | 629 | 997 | 989 | 1108 |
|  |  | ${ }^{4} \mathrm{~T}_{2 \mathrm{~g}}$ | 6622 | 5785 | 5402 | 5692 |
|  |  |  | 6631 | 7308 | 7709 | 7897 |
|  |  |  | 8687 | 8775 | 8677 | 8487 |
|  |  | ${ }^{4} \mathrm{~A}_{2}$ | 15369 | 15418 | 15461 | 15446 |
|  | ${ }^{4} \mathrm{P}$ | ${ }^{4} \mathrm{~T}_{1 \mathrm{~g}}$ | 22259 | 21747 | 21538 | 21392 |
|  |  |  | 23281 | 22321 | 22238 | 22774 |
|  |  |  | 23372 | 25497 | 26402 | 25896 |
| 2 | ${ }^{2} \mathrm{G}+{ }^{2} \mathrm{P}$ |  | 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 S7. Relative CASPT2 energies (in $\mathrm{cm}^{-1}$ ) of all quartet and the 12 lowest doublet states for the crystallographically independent cobalt(॥) centers in 3C and 3L

| $2 S+1$ | Term | Subterm | 3C-Co1 | 3C-Co2 | 3L-Co1 | 3L-Co2 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 4 | ${ }^{4} \mathrm{~F}$ | ${ }^{4} \mathrm{~T}_{1 \mathrm{~g}}$ | 0 | 0 | 0 | 0 |
|  |  |  | 841 | 506 | 580 | 708 |
|  |  |  | 838 | 946 | 823 | 982 |
|  |  | ${ }^{4} \mathrm{~T}_{2 \mathrm{~g}}$ | 7320 | 6894 | 6359 | 6699 |
|  |  |  | 7346 | 8444 | 8702 | 8978 |
|  |  |  | 9998 | 9942 | 9672 | 9499 |
|  |  | ${ }^{4} \mathrm{~A}_{2}$ | 17640 | 17636 | 17566 | 17548 |
|  | ${ }^{4} \mathrm{P}$ | ${ }^{4} \mathrm{~T}_{1 \mathrm{~g}}$ | 20104 | 19287 | 19039 | 18853 |
|  |  |  | 20628 | 20137 | 20011 | 20604 |
|  |  |  | 20714 | 23257 | 24219 | 23628 |
| 2 | ${ }^{2} \mathrm{G}+{ }^{2} \mathrm{P}$ |  | 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 S8. Relative RASSI-SO energies (in $\mathrm{cm}^{-1}$ ) of the six lowest Kramers doublets of the ${ }^{4} \mathrm{~T}_{1 \mathrm{~g}}$ ground multiplet for the crystallographically independent cobalt(॥) centers in 3C and 3L

| Term | Subterm | KD | 3C-Co1 | 3C-Co2 | 3L-Co1 | 3L-Co2 |
| :---: | ---: | :---: | ---: | ---: | ---: | ---: |
| ${ }^{4} \mathrm{~F}$ | ${ }^{4} \mathrm{~T}_{1 \mathrm{~g}}$ | 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 |
|  |  | 1387 | 1437 | 1359 | 1457 |  |



Figure S32. Representation of the magnetic axes for the ground state Kramers doublet ( $S_{\text {eff }}=1 / 2$; 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).
3 A B C D

$\qquad$


3C-Co2/C2


Scheme S1. Graphical definition of 12-membered spin rings of the type $[\cdots \mathrm{A} \cdots \mathrm{B} \cdots \mathrm{C} \cdots \mathrm{D} \cdots]_{3}$ 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 12membered spin ring coupling scheme together with a positive coupling constant for the Lines model $\left(J_{i j}>0\right)$ 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).


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