Electronic Supplementary Information

Tuning of the exchange interaction and the Curie temperature by mixed crystal formation of the bridging anionic ligands

Tristan Neumann,^a Michał Rams,^{b*} Zbigniew Tomkowicz,^b Inke Jess,^a and Christian Näther ^{a*}

^a Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel, Max-Eyth-Str. 2, 24118, Kiel, Germany.
Tel: +49 431 880 2092; E-mail: cnaether@ac.uni-kiel.de

^b Institute of Physics, Jagiellonian University, Łojasiewicza 11, 30348 Kraków, Poland. E-mail: m.rams@uj.edu.pl

Content		
1	Experimental	4
1.1	Synthesis	4
1.2	Methods	4
Fig. S1	$ \begin{array}{llllllllllllllllllllllllllllllllllll$	6
Fig. S2	Calculated XRPD pattern of Co(NCS) ₂ (pyridine) ₄ and Co(NCSe) ₂ (pyridine) ₄ .	6
Fig. S3	Experimental and calculated XRPD pattern of $Co(NCS)_2(pyridine)_4$ and $Co(NCSe)_2(pyridine)_4$.	7
Fig. S4	Experimental and calculated XRPD pattern of $[Co(NCS)_2(pyridine)_2]_n$ and $[Co(NCSe)_2(pyridine)_2]_n$.	7
Fig. S5	Experimental XRPD pattern of physical mixtures of $Co(NCS)_2(pyridine)_4$ and $Co(NCSe)_2(pyridine)_4$ in different $NCSe^-$: NCS^- ratios and of the pure compounds.	8
Fig. S6	Experimental XRPD pattern of physical mixtures of $[Co(NCS)_2(pyridine)_2]_n$ and $[Co(NCSe)_2(pyridine)_2]_n$ in different NCSe ⁻ : NCS ⁻ ratios and of the pure compounds.	8
Fig. S7	IR spectra of physical mixtures of $Co(NCS)_2(pyridine)_4$ and $Co(NCSe)_2(pyridine)_4$ in different NCSe ⁻ : NCS ⁻ ratios and of the pure compounds.	8
Fig. S8	IR spectra of physical mixtures of $[Co(NCS)_2(pyridine)_2]_n$ and $[Co(NCSe)_2(pyridine)_2]_n$ in different NCSe ⁻ : NCS ⁻ ratios and of the pure compounds.	9
Fig. S9	Experimental XRPD pattern of mixed crystals with the composition $Co(NCSe)_x(NCS)_{2-x}(pyridine)_4$ and of physical mixtures of $Co(NCSe)_2(pyridine)_4$ and $Co(NCS)_2(pyridine)_4$ with the same NCSe : NCS ratio.	9
Tab. S1	Results of x (S content) determination by EDX using Co-K, S-K and Se-L energies for mixed crystals with the nominal composition $Co(NCS)_x(NCSe)_{2-x}(pyridine)_4$ at different crystallites from the same batch.	9
Tab. S2	Selected crystal data and details of the single crystal structure refinements. Please note that the crystals were obtained from the filtrate under kinetic control, leading, in contrast to the microcrystalline powders, to a larger distribution of the S:Se ratio.	10
Fig. S10	Crystal structures of mixed crystals with the composition $Co(NCS)_x(NCSe)_{2-x}(pyridine)_4$ with x with labeling and displacement ellipsoids drawn at the 50% probability level.	11
Fig. S11	DTG, TG and DTA curves of $Co(NCS)_x(NCSe)_{2-x}(pyridine)_4$ (x = 0.5, 1, 1.5).	12
Fig. S12	Experimental XRPD pattern of mixed crystals prepared by thermal decomposition with the composition $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ and of	12

physical mixtures of $[Co(NCSe)_2(pyridine)_2]_n$ and $Co(NCS)_2(pyridine)_2]_n$ with the same NCS : NCSe ratio.

- Tab. S3Results of the EDX measurements of mixed crystals with the composition13 $[Co(NCSe)_x(NCS)_{2-x}(pyridine)]_n.$
- Tab. S4Results of the EDX measurements of mixed crystals with the composition13 $[Co(NCSe)_x(NCS)_{2-x}(pyridine)_2]_n.$
- Fig. S13 Experimental XRPD pattern of mixed crystals prepared from solution with the 13 composition $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ and of physical mixtures of $[Co(NCS)_2(pyridine)_2]_n$ and $[Co(NCSe)_2(pyridine)_2]_n$ with the same NCS : NCSe ratio.
- Fig. S14 Experimental XRPD pattern of mixed crystals prepared from solution and 14 annealing with the composition $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ and of physical mixtures of $[Co(NCS)_2(pyridine)_2]_n$ and $[Co(NCSe)_2(pyridine)_2]_n$ with the same NCS⁻ : NCSe⁻ ratio.
- Fig. S15 Magnetic susceptibility χ measured at 1 kOe for 14 $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ samples obtained from annealing (a) and solution (s), shown as the χT product. Lines are to guide the eye.
- Fig. S16 Zero-field cooled (lines) and field cooled (points) susceptibility measured at 100 15 Oe for $Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ prepared by annealing and in solution.
- Fig. S17 Magnetization hysteresis loops measured at 1.8 K for samples of 15 $Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ prepared by annealing and in solution.
- Fig. S18 Ac magnetic susceptibility, for $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ samples. 16
- Fig. S19 Analysis of the low temperature susceptibility measured at 100 Oe for $Co(NCS)_x(NCSe)_{2-x}$ (pyridine)₂]_n samples using the Ising chain model.
- Tab. S5 Estimation of the exchange interaction *J*, and the *g*-factor for the series of 17 $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ samples, obtained from the analysis of specific heat and susceptibility data.
- Fig. S20 Derivative $d\chi/dT$ of susceptibility $\chi(T)$ curves measured at 100 Oe following 18 field cooling for $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ samples obtained from annealing and solution.
- Fig. S21 Critical temperature T_c determined as the position of the $d\chi/dT$ minimum, shown 18 as a function of the thiocyanate content x for compounds with the composition $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ obtained from solution and by annealing.
- Fig. S22 Exchange interaction *J* obtained for samples prepares from solution (black 19 points), and by annealing (red), determined using specific heat data (triangles) and susceptibility (circles).

1 Experimental

1.1 Synthesis

General

 $Co(NO_3)_2 \cdot 6H_2O$ and KSCN were obtained from Merck and KSeCN was obtained from Alfa Aesar. All salts and solvents were used without further purification.

Synthesis of $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$.

Crystalline powders of $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ were prepared by mixing $Co(NO_3)_2 \cdot 6H_2O$ (1.0 mmol, 291.0 mg) with a stoichiometric amount of KSCN and KSeCN in the desired ratio(1:3, 1:1 and 3:1) in EtOH for 4h. The resulting precipitate of KNO₃ was removed and pyridine (1.0 mmol, 80.7 µL) was added to the filtrate, which was then stirred for 2d. The resulting precipitate of the mixed crystals was filtered off and dried overnight.

Samples of $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ were also obtained through annealing of mixed crystals of the composition of $Co(NCS)_x(NCSe)_{2-x}(pyridine)_4$ at 110°C for 8 h.

Synthesis of $Co(NCS)_x(NCSe)_{2-x}(pyridine)_4$.

Crystalline powders were obtained by stirring of $Co(NO_3)_2 \cdot 6H_2O$ (1.0 mmol, 291.0 mg) with a stoichiometric amount of KSCN and KSeCN in the desired ratio in EtOH (4.0 mL). The precipitate of KNO₃ was filtered off and pyridine (1.0 mL) was added to the filtrate in an excess under stirring. The final residue was filtered.

Single crystals suitable for single crystal x-ray-diffraction were obtained by the reaction of $Co(NO_3)_2$ \cdot 6 H₂O (1.0 mmol, 291.0 mg) with different ratios of KSeCN and KSCN in the desired ratio The resulting precipitate of KNO₃ was filtered off and an excess of pyridine was added to the filtrate. From the filtrate crystals were obtained within 3 d.

1.2 Methods

Single crystal X-ray diffraction.

Data collection was performed using a STOE Imaging Plate Diffraction System. IPDS-2. For all data sets a numerical absorption correction was performed using X-Red and X-Shape from STOE. All non-hydrogen atoms were refined anisotropic. The C-H H atoms were positioned with idealized geometry and were refined isotropic with $U_{iso}(H) = 1.2 U_{eq}(C)$ using a riding model. The thiocyanate respectively selenocyanate anion was refined without any restraints. The position of the S, respectively Se atoms can be resolved and their site occupation factor was refined leading to reasonable anisotropic displacement parameters that are comparable to that of the other atoms. The position of the C and the N atom of the anionic ligand cannot be resolved.

X-ray powder diffraction (XRPD).

All powder diffraction measurements were performed on a STOE Transmission Powder Diffraction System (Stadi-P) with Cu-K_{α} radiation and a Dectris Mythen 1K detector with a Johannson-type-Ge(111) monochromator from STOE & CIE.

Differential thermoanalysis and thermogravimetry (DTA-TG).

The DTA-TG measurements were performed in Al_2O_3 crucibles under a dynamic nitrogen atmosphere (purity: 5.0) with a flow rate of 75 mL min⁻¹ using a STA-PT1000° thermobalance from Linseis. The instrument was calibrated using standard reference materials. All measurements were performed with a flow rate of 75 mL·min⁻¹ and were corrected for buoyancy.

IR-Spectroscopy.

All IR spectra were recorded using an ATI Mattson Genesis Series FTIR Spectrometer, control software: WINFIRST, from ATI Mattson (Midland, On, Canada).

Magnetic measurements.

Quantum Design MPMS XL5 squid-type magnetometer was used. The powder samples were lightly pressed to form a pellet with some PTFE tape to prevent grain rotation in magnetic field. The pellets were oriented with flat along the field to minimize the demagnetization effect.

Specific heat measurements.

The relaxation method of Quantum Design PPMS was used. The samples were lightly pressed with no binder to form a pellet and fixed with Apiezon N grease to the microcalorimeter. The specific heat of the grease was measured and subtracted for each sample.



Fig. S1. Calculated XRPD pattern of $[Co(NCS)_2(pyridine)_2]_n$ (top) and $[Co(NCSe)_2(pyridine)_2]_n$ (bottom). The powder pattern of the selenocyanate compound was calculated based on the results of a Rietveld refinement.



Fig. S2. Calculated XRPD pattern of Co(NCS)₂(pyridine)₄ (top) and Co(NCSe)₂(pyridine)₄ (bottom).



Fig. S3. Experimental (top) and calculated (bottom) XRPD pattern of Co(NCS)₂(pyridine)₄ (left) Co(NCSe)₂(pyridine)₄ (right).

Fig. S4. Experimental (top) and calculated (bottom) XRPD pattern of $[Co(NCS)_2(pyridine)_2]_n$ (left) and $[Co(NCSe)_2(pyridine)_2]_n$ (right). The powder pattern for the selenocyanate compound was calculated on the basis of a Rietveld refinement.

Fig. S5. Experimental XRPD pattern of physical mixtures of $Co(NCS)_2(pyridine)_4$ and $Co(NCSe)_2(pyridine)_4$ in different NCS⁻ : NCSe⁻ ratios (blue) and of the pure compounds (black).

Fig. S6. Experimental XRPD pattern of physical mixtures of $[Co(NCS)_2(pyridine)_2]_n$ and $[Co(NCSe)_2(pyridine)_2]_n$ in different NCS⁻ : NCSe⁻ ratios (blue) and of the pure compounds (black).

Fig. S7. IR spectra of physical mixtures of $Co(NCSe)_2(pyridine)_4$ and $Co(NCS)_2(pyridine)_4$ in different $NCSe^-$: NCS^- ratios (blue) and of the pure compounds (black).

Fig. S8. IR spectra of physical mixtures of $[Co(NCSe)_2(pyridine)_2]_n$ and $[Co(NCS)_2(pyridine)_2]_n$ in different NCSe⁻ : NCS⁻ ratios (blue) and of the pure compounds (black).

Fig. S9. Experimental XRPD pattern of mixed crystals with the composition $Co(NCS)_x(NCSe)_{2-x}(pyridine)_4$ (black) and of physical mixtures of $Co(NCSe)_2(pyridine)_4$ and $Co(NCS)_2(pyridine)_4$ with the same $NCSe^-$: NCS^- ratio (blue).

Tab. S1. Results of x (S content) determination by EDX using Co-K, S-K and Se-L energies for mixed crystals with the nominal composition $Co(NCS)_x(NCSe)_{2-x}(pyridine)_4$ at different crystallites from the same batch.

	x = 0.5	x = 1.0	x = 1.5
sample 1	0.57	1.02	1.46
sample 2	0.57	1.04	1.44
sample 3	0.56	1	1.46
sample 4	0.58	1.01	1.46
Bulk	0.64	1.05	1.49
Ø	0.58	1.02	1.46

compound	1-Co-Sample1	1-Co-Sample2	2-Co-Sample1
Formula	$C_{22}H_{20}CoN_6S_{1.50}Se_{0.50}$	$C_{22}H_{20}CoN_6S_{1.50}Se_{0.50}$	$C_{22}H_{20}CoN_6S_{0.98}Se_{1.02}$
$MW / g mol^{-1}$	515.06	515.06	539.33
crystal system	monoclinic	Monoclinic	monoclinic
space group	C2/c	C2/c	C2/c
<i>a</i> / Å	12.3427(5)	12.3437(5)	12.3704(5)
<i>b</i> / Å	13.0507(4)	13.0497(4)	13.1326(6)
<i>c</i> / Å	14.9969(6)	15.0003(7)	15.0005(6)
α / \circ	90	90	90
β/\circ	107.661(3)	107.640(3)	108.016(3)
γ/\circ	90	90	90
V/Å ³	2301.86(15)	2302.66(16)	2317.43(17)
T/K	170(2)	170(2)	170(2)
Ζ	4	4	4
$D_{\rm calc}$ / g cm ⁻³	1.486	1.486	1.546
μ / mm^{-1}	1.697	1.697	2.452
$\theta_{\rm max}$ / deg	28.002	28.001	27.994
measured refl.	13360	13897	13979
unique refl.	2772	2774	2792
$R_{\rm int}$	0.0336	0.0386	0.0629
refl. $[F_0 > 4\sigma(F_0)]$	2305	2210	2431
parameters	153	152	152
sof S	0.748(3)	0.744(3)	0.494(3)
$R_1 [F_0 > 4\sigma(F_0)]$	0.0455	0.0410	0.0323
wR_2 [all data]	0.1148	0.0918	0.0676
GOF	1.061	1.065	1.075
$\Delta ho_{ m max/min}$ / e Å ⁻³	0.359/-0.400	0.330/ -0.321	0.280/-0.248

Tab. S2. Selected crystal data and details of the single crystal structure refinements. Please note that the crystals were obtained from the filtrate under kinetic control, leading, in contrast to the microcrystalline powders, to a larger distribution of the S:Se ratio.

compound	2-Co-Sample2	3-Co-Sample1	3-Co-Sample2
Formula	C22H20CoN6S1.11Se0.89	C22H20CoN6S0.64Se1.36	C ₂₂ H ₂₀ CoN6S _{0.68} Se _{1.32}
MW / g mol ⁻¹	533.35	555.04	553.40
crystal system	monoclinic	Monoclinic	monoclinic
space group	C2/c	C2/c	C2/c
<i>a</i> / Å	12.3648(5)	12.3895(3)	12.3922(7)
<i>b</i> / Å	13.1112(4)	13.1754(3)	13.1777(4)
<i>c</i> / Å	15.0007(6)	15.0176(4)	15.0173(8)
α / °	90	90	90
β/\circ	108.097(3)	108.230(2)	108.244(4)
γ/\circ	90	90	90
$V/Å^3$	2311.57(15)	2328.38(10)	2329.1(2)
T/K	170(2)	170(2)	170(2)
Ζ	4	4	4
$D_{\rm calc}$ / g cm ⁻³	1.533	1.583	1.578
μ / mm^{-1}	2.269	2.934	2.882
$\theta_{\rm max}$ / deg	28.003	28.004	28.000
measured refl.	16009	18308	9945
unique refl.	2786	2810	2797
$R_{\rm int}$	0.0588	0.0300	0.0401
refl. $[F_0 > 4\sigma(F_0)]$	2485	2523	2414
parameters	153	152	152
sof S	0.556(3)	0.320(3)	0.339(5)
$R_1 [F_0 > 4\sigma(F_0)]$	0.0368	0.0346	0.0345
wR_2 [all data]	0.0953	0.0913	0.0745
GOF	1.040	1.090	1.039
$\Delta ho_{ m max/min}$ / e Å ⁻³	0.380/-0.457	0.379/-0.484	0.314/-0.372

Fig. S10. Crystal structures of mixed crystals with the composition $Co(NCS)_x(NCSe)_{2-x}(pyridine)_4$ with labeling and displacement ellipsoids drawn at the 50% probability level.

Fig. S11. DTG, TG and DTA curves of $Co(NCS)_x(NCSe)_{2-x}(pyridine)_4$ with x = 1.5 (left), 1 (middle) and 1.5 (right).

Fig. S12. Experimental XRPD pattern of mixed crystals prepared by thermal decomposition with the composition $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ (black) and of physical mixtures of $[Co(NCS)_2(pyridine)_2]_n$ and $[Co(NCSe)_2(pyridine)_2]_n$ with the same NCS^- : $NCSe^-$ ratio (blue).

Tab. S3. Results of the EDX measurements of mixed crystals with the composition $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ on different crystallites of the same batch from thermal decomposition measured on Co-K, S-K and Se-L.

	x = 0.5	x = 1.0	x = 1.5
sample 1	0.56	1.02	1.5
sample 2	0.57	1.01	1.46
sample 3	0.55	1.02	1.47
sample 4	0.57	1.01	1.48
Bulk	0.61	1.02	1.47
Ø	0.57	1.02	1.48

Tab. S4. Results of the EDX measurements of mixed crystals with the composition $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ on different crystallites of the same batch from solution measured on Co-K, S-K and Se-L.

	x = 0.5	x = 1.0	x = 1.5
sample 1	0.59	1.09	1.51
sample 2	0.6	1.11	1.51
sample 3	0.61	1.09	1.51
sample 4	0.59	1.09	1.42
Bulk	0.64	1.08	1.51
Ø	0.61	1.09	1.49

Fig. S13. Experimental XRPD pattern of mixed crystals prepared from solution with the composition $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ (black) and of physical mixtures of $[Co(NCS)_2(pyridine)_2]_n$ and $[Co(NCSe)_2(pyridine)_2]_n$ with the same NCS⁻ : NCSe⁻ ratio (blue).

Fig. S14. Experimental XRPD pattern of mixed crystals prepared from solution (black) and annealing (red) with the composition $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ and of physical mixtures of $[Co(NCS)_2(pyridine)_2]_n$ and $[Co(NCSe)_2(pyridine)_2]_n$ with the same NCS^- : $NCSe^-$ ratio (blue).

Fig. S15. Magnetic susceptibility χ measured at 1 kOe for $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ samples obtained from annealing (a) and solution (s), shown as the χT product. Lines are to guide the eye.

Fig. S16. Zero-field cooled (lines) and field cooled (points) susceptibility measured at 100 Oe for $Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ samples.

Fig. S17. Magnetization hysteresis loops measured at 1.8 K for samples of $Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$. Lines are to guide the eye.

Fig. S18. Ac magnetic susceptibility, in-phase component (top) and out-of-phase component (bottom) for $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ samples. Lines are to guide the eye.

Fig. S19. Analysis of the low temperature susceptibility measured at 100 Oe for $Co(NCS)_x(NCSe)_{2-x}$ (pyridine)₂]_n samples using the Ising chain model. The data range used in the quantitative analysis and shown in Fig. 3 is between dashed horizontal lines. The straight solid lines are fitted.

The reason to omit the low *T* data is: (i) to avoid the influence of the interchain interaction and related magnetic ordering, (ii) to avoid the demagnetization effect, (iii) to avoid a saturation of susceptibility by magnetic field. On the other side, the high *T* data are omitted because: (iv) the excited Kramers doublet of Co^{2+} is gradually populated as *T* increases, which causes deviation from the s = 1/2 model, (v) the influence of the perpendicular susceptibility in the Ising model (in respect to the J_z Ising exchange axis) increases at higher *T*. The restriction of the data range allows us keeping the model simple and limiting the number of simultaneously fitted parameters to only two: the exchange interaction *J* and the parallel *g*-factor $g_z = g_{par}$. In such case the Ising chain model predicts the average powder susceptibility

 $\chi T = (1/3) N_A \mu_B^2 s(s+1) g_{par}^2 \exp[J/(2k_B T)] / (3k_B)$

at low temperature limit. The linear dependence of $\ln(\chi T) vs (1/T)$ is a test if the above model works. It is better to use the same range of χT for all samples in the analysis, instead of using the same range of *T*, because χT is the correlation length. Even if obtained values of *J* depend slightly on the used range, the comparison between the samples can be done.

Tab. S5 Estimation of the exchange interaction *J*, and the *g*-factor for the series of $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ samples, obtained from the analysis of specific heat and susceptibility data. For comparison, published data for $Co(NCS)_2(pyridine)_2$ (x = 2) are: *g* = 7.0 from HF-ESR, *g* = 8.3, 8.5 from *ab-initio* calculations, *J* = 28 K from $\chi(T)$ using a more general model, *J* = 27.6 K from *C*(*T*). [Phys.Chem.Chem.Phys., 2017, 19, 24534]

nominal x	g_{par}	<i>J/2</i> (K)	<i>J</i> /2 (K)
		from $\ln(\chi T)(1/T)$	from $C(T)$
2	7.73(10)	14.1(2)	13.8
1.5 (s)	7.5(2)	15.6(3)	14.5
1.5 (a)	7.7(2)	14.7(3)	14.0
1.0 (s)	7.5(2)	17.1(4)	15.4
1.0 (a)	7.3(2)	16.9(3)	14.8
0.5 (s)	7.5(2)	17.9(3)	16.3
0.5 (a)	7.4(2)	18.1(3)	16.4
0	7.45(10)	18.4(3)	17.8

Fig. S20. Derivative $d\chi/dT$ of susceptibility $\chi(T)$ curves measured at 100 Oe following the field cooling for $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ samples obtained from annealing (a) and solution (s).

Fig. S21. Critical temperature T_c determined as the position of the $d\chi/dT$ minimum, shown as a function of the thiocyanate content x for compounds with the composition $[Co(NCS)_x(NCSe)_{2-x}(pyridine)_2]_n$ obtained from solution and by annealing. These T_c values are a bit less precise than results from C(T) data, shown in the main text, because they depend on the field used to measure χ .

Fig. S22. Exchange interaction *J* obtained for samples prepares from solution (black), and by annealing (red), determined using specific heat data (triangles) and susceptibility (circles).

The values of J were also determined by fitting C(T) above T_c by the sum of the lattice contribution and the magnetic contribution that is given by analytical Fisher's solution

$$C_{magn}(T) = N_A k_B \left[J/(4k_B T) \right]^2 / \cosh^2[J/(4k_B T)]$$

for the s = 1/2 spin Ising chain Hamiltonian $H = -J \sum_{n} s^{z} s^{n} s^{z} s^{n+1}$. Obtained *J* values depend on the used range of *T* and on assumptions about the lattice contribution. For this reason they are less precise than *J* obtained using $\ln(\chi T)$ data, shown in the main text in Fig. 4.