

Supporting Information

**Synthesis, Structures and Magnetic Properties of Fe(II) and
Co(II) Thiocyanato Coordination Compounds: On the
Importance of the Diamagnetic Counterparts for Structure
Determination.**

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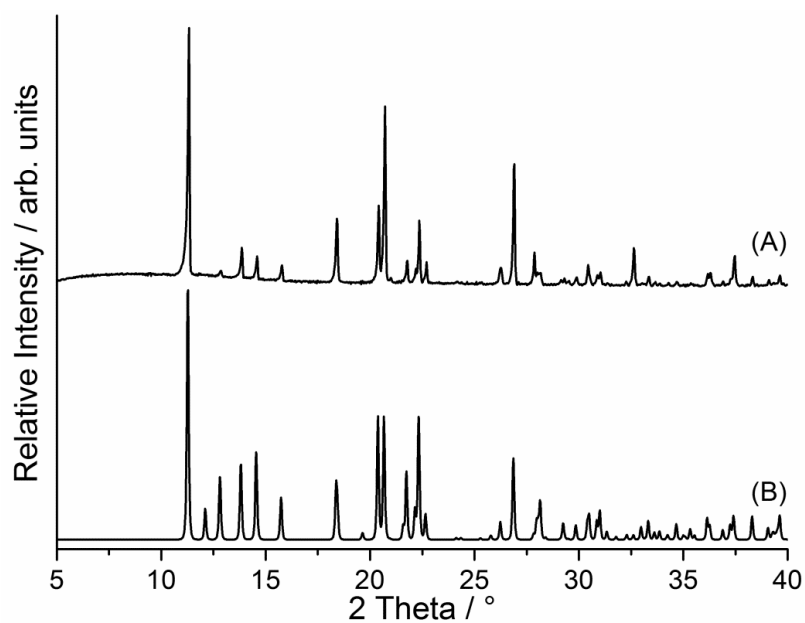


Fig. S1. Experimental XRPD pattern of **1-Co** (A) together with the powder pattern calculated from single crystal data (B).

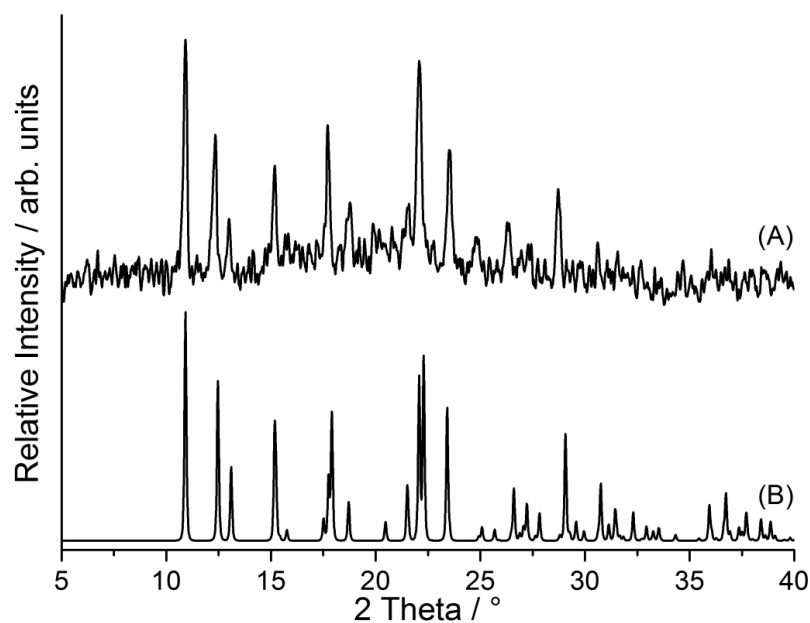


Fig. S2. Experimental XRPD pattern of **2-Co** (A) together with the powder pattern calculated from single crystal data (B).

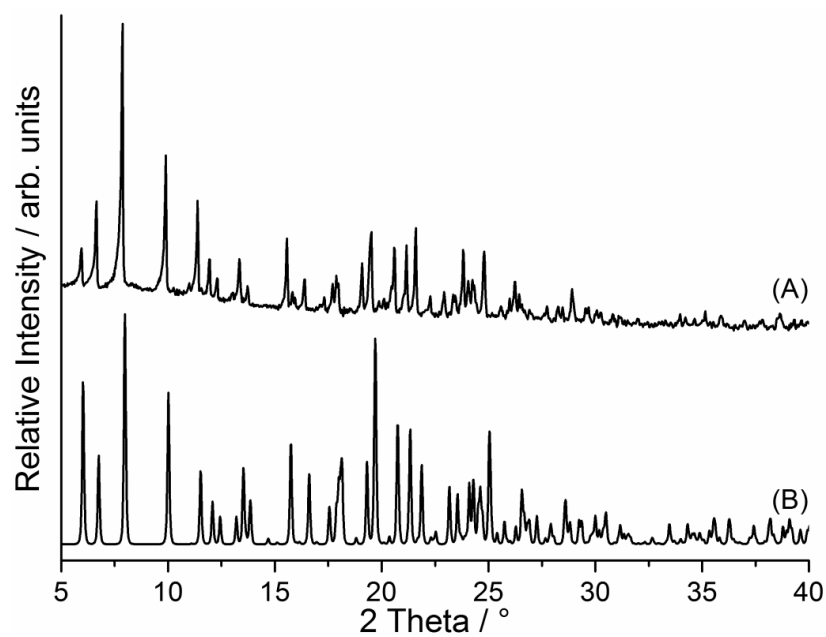


Fig. S3. Experimental XRPD pattern of **3-Co** (A) together with the powder pattern calculated from single crystal data (B).

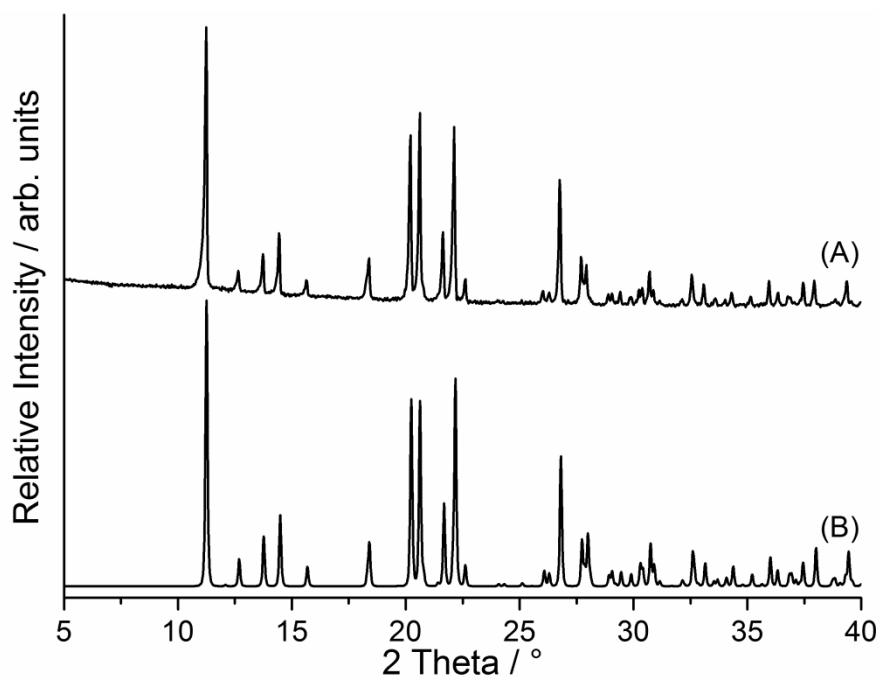


Fig. S4. Experimental XRPD pattern of **1-Fe** (A) together with the powder pattern calculated from single crystal data (B).

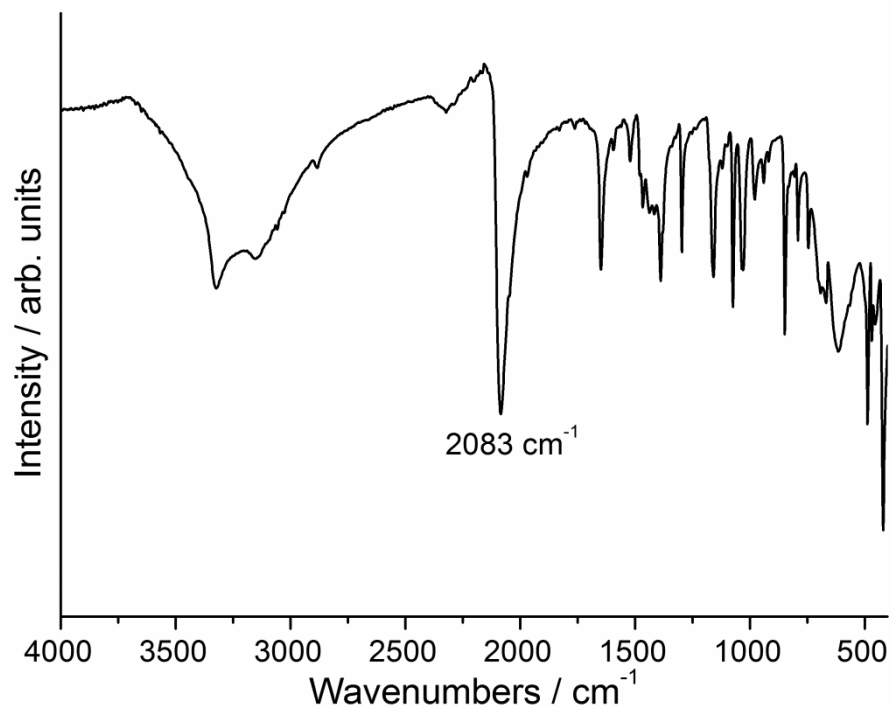


Fig. S5. IR spectrum of $\text{Co(NCS)}_2(2\text{-methylpyrazine})_2(\text{H}_2\text{O})_2$ (**1-Co**).

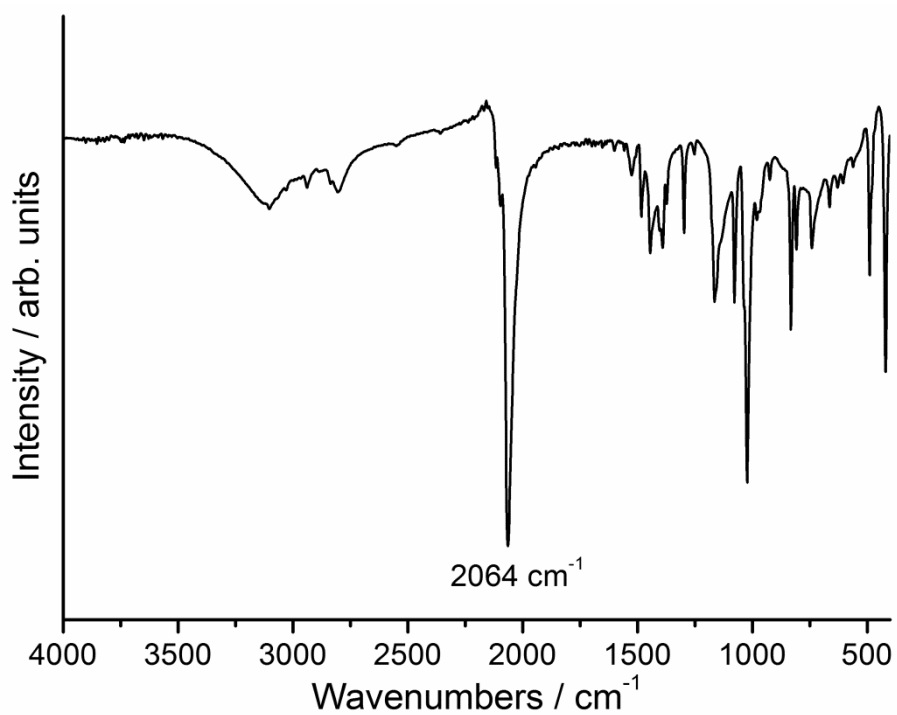


Fig. S6. IR spectrum of $\text{Co(NCS)}_2(2\text{-methylpyrazine})_2(\text{CH}_3\text{OH})_2$ (**2-Co**).

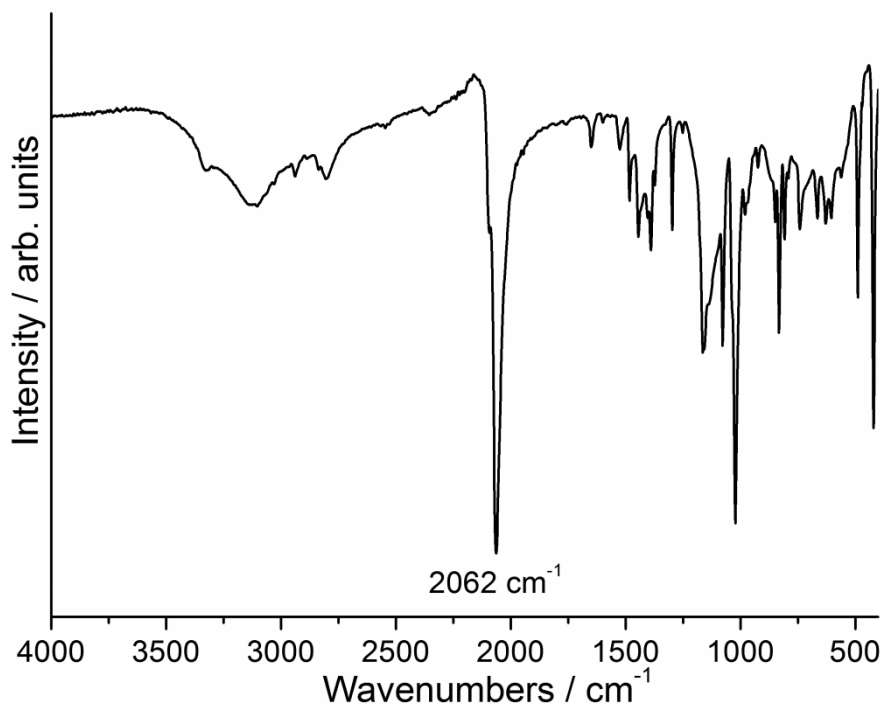


Fig. S7. IR spectrum of $\text{Co}(\text{NCS})_2(2\text{-methylpyrazine})_4 \cdot 2\text{-methylpyrazine}$ solvate (**3-Co**).

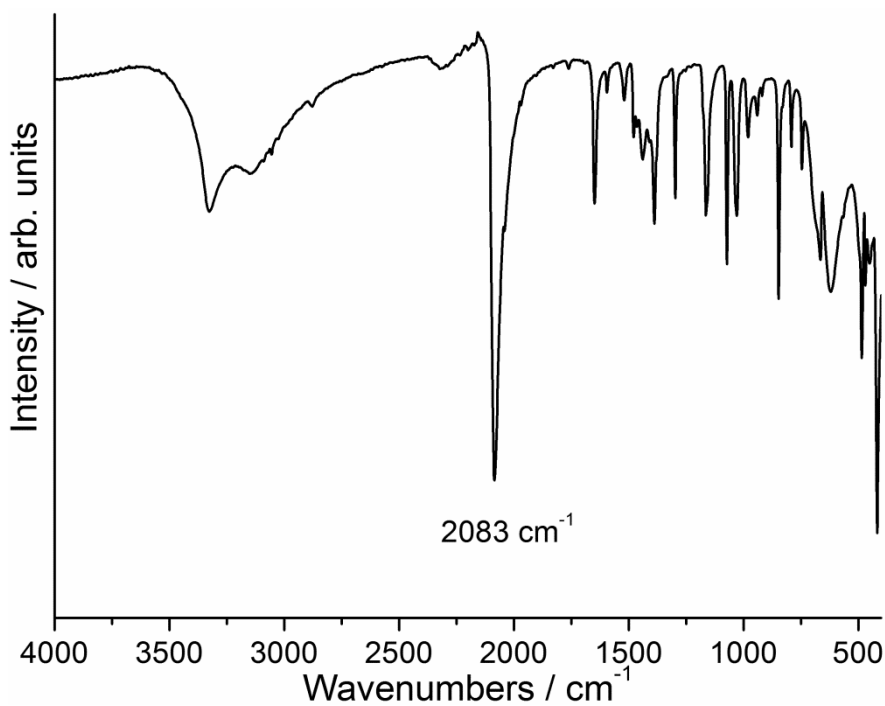


Fig. S8. IR spectrum of $\text{Fe}(\text{NCS})_2(2\text{-methylpyrazine})_2(\text{H}_2\text{O})_2$ (**1-Fe**).

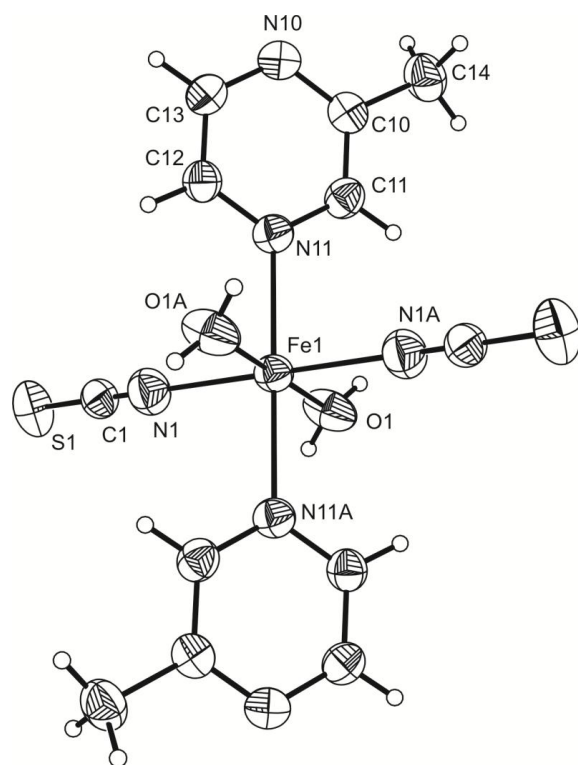


Fig. S9. ORTEP plot of $\text{Fe}(\text{NCS})_2(2\text{-methylpyrazine})_2(\text{H}_2\text{O})_2$ (**1-Fe**). Symmetry transformation used to generate equivalent atoms: $A = -x, -y, -z + 1$.

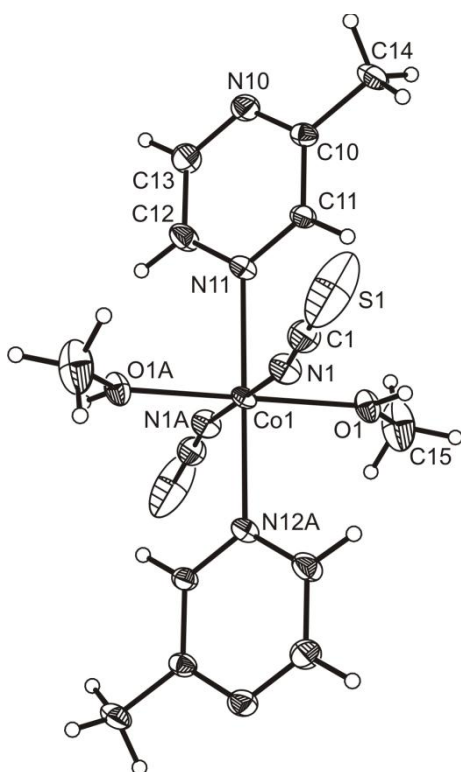


Fig. S10. ORTEP plot of $\text{Co}(\text{NCS})_2(2\text{-methylpyrazine})_2(\text{CH}_3\text{OH})_2$ (**2-Co**). Symmetry transformation used to generate equivalent atoms: $A = -x, -y, -z + 1$.

Table S1. Selected bond lengths / Å and angles / ° for $\text{Fe}(\text{NCS})_2(2\text{-methylpyrazine})_2(\text{H}_2\text{O})_2$ (**1-Fe**) and $\text{Co}(\text{NCS})_2(2\text{-methylpyrazine})_2(\text{CH}_3\text{OH})_2$ (**2-Co**). Symmetry transformation used to generate equivalent atoms: $A = -x, -y, -z + 1$.

	1-Fe	2-Co
M(1)-N(1)	2.1104(15)	2.063(3)
M(1)-N(11)	2.2205(12)	2.176(2)
M(1)-O(1)	2.1258(11)	2.103(2)
N(1A)-M(1)-N(1)	180.0	180.00(14)
N(1A)-M(1)-O(1)	91.38(6)	93.02(10)
N(1)-M(1)-O(1)	88.62(6)	86.98(10)
N(1)-M(1)-N(11)	90.46(5)	88.60(10)
N(1)-M(1)-N(11A)	89.54(5)	91.40(10)
O(1)-M(1)-O(1A)	180.0	180.0
O(1)-M(1)-N(11A)	88.90(5)	88.75(9)
O(1)-M(1)-N(11)	91.10(5)	91.25(9)

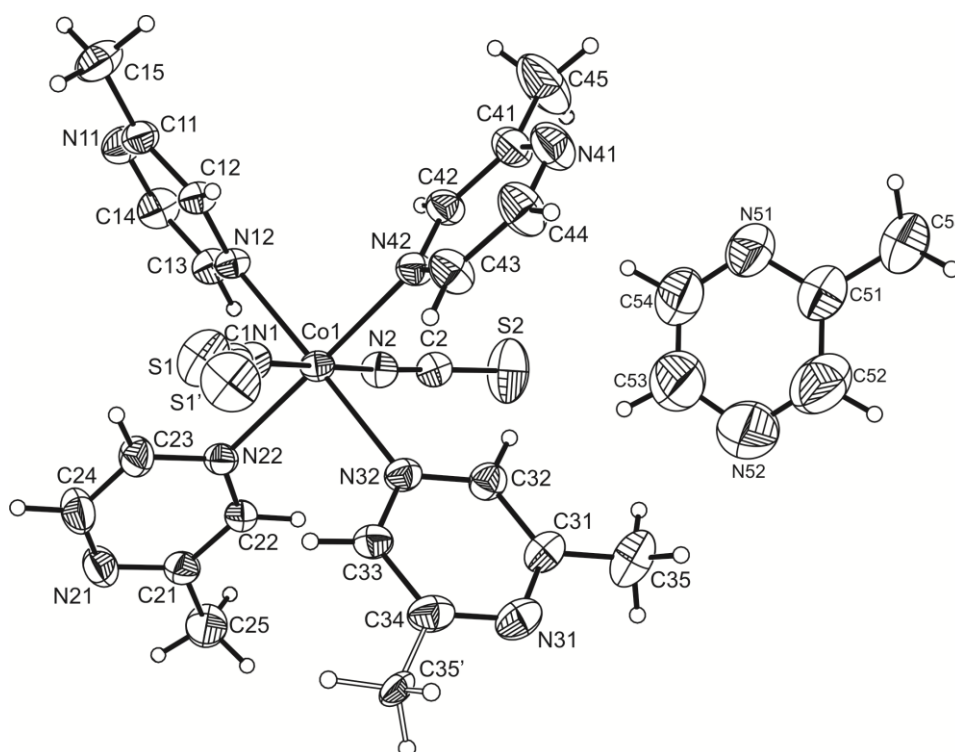


Fig. S11. ORTEP plot of $\text{Co}(\text{NCS})_2(2\text{-methylpyrazine})_4 \cdot 2\text{-methylpyrazine}$ solvate (**3-Co**).

The disordering of the non-coordinated 2-methylpyrazine ligand was omitted for clarity.

Table S2. Selected bond lengths / Å and angles / ° for $\text{Co}(\text{NCS})_2(2\text{-methylpyrazine})_4 \cdot 2\text{-methylpyrazine}$ solvate (**3-Co**).

compounds	3-Co
Co(1)-N(1)	2.063(3)
Co(1)-N(2)	2.066(2)
Co(1)-N(12)	2.191(2)
Co(1)-N(22)	2.193(2)
Co(1)-N(32)	2.186(2)
Co(1)-N(42)	2.168(2)
N(1)-Co(1)-N(2)	179.43(10)
N(1)-Co(1)-N(42)	89.79(10)
N(2)-Co(1)-N(32)	89.68(10)
N(42)-Co(1)-N(32)	89.37(9)
N(42)-Co(1)-N(12)	92.03(9)
N(32)-Co(1)-N(12)	178.57(9)
N(42)-Co(1)-N(22)	179.08(9)
N(32)-Co(1)-N(22)	91.38(9)
N(2)-Co(1)-N(42)	89.85(10)
N(1)-Co(1)-N(32)	89.88(10)
N(1)-Co(1)-N(12)	90.43(9)
N(2)-Co(1)-N(12)	90.02(9)
N(1)-Co(1)-N(22)	89.69(10)
N(2)-Co(1)-N(22)	90.67(10)
N(12)-Co(1)-N(22)	87.22(9)

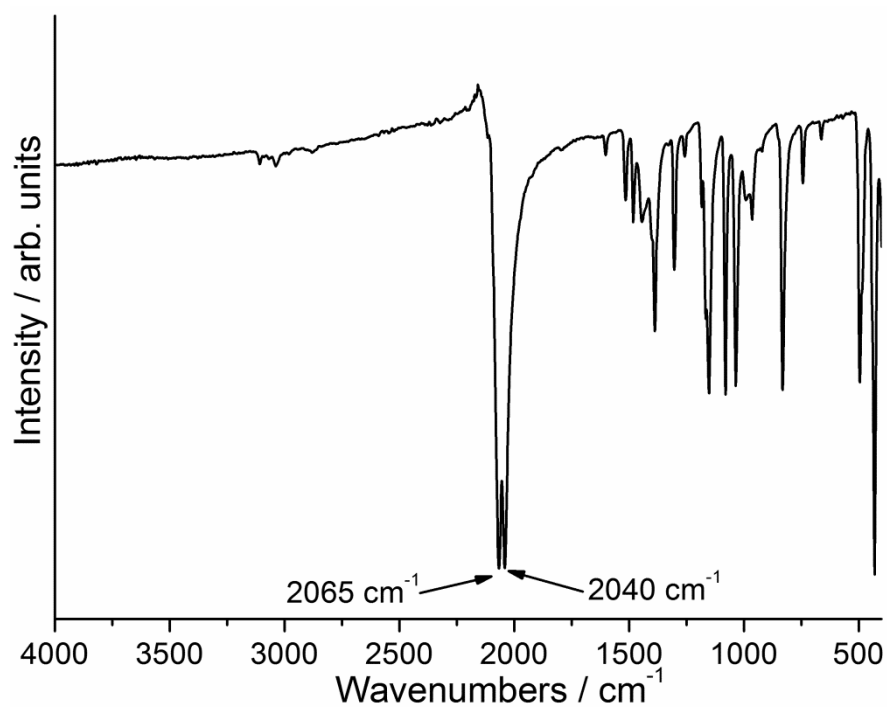


Fig. S12. IR spectrum of the residue, which was obtained in the first heating step of compound **1-Co**.

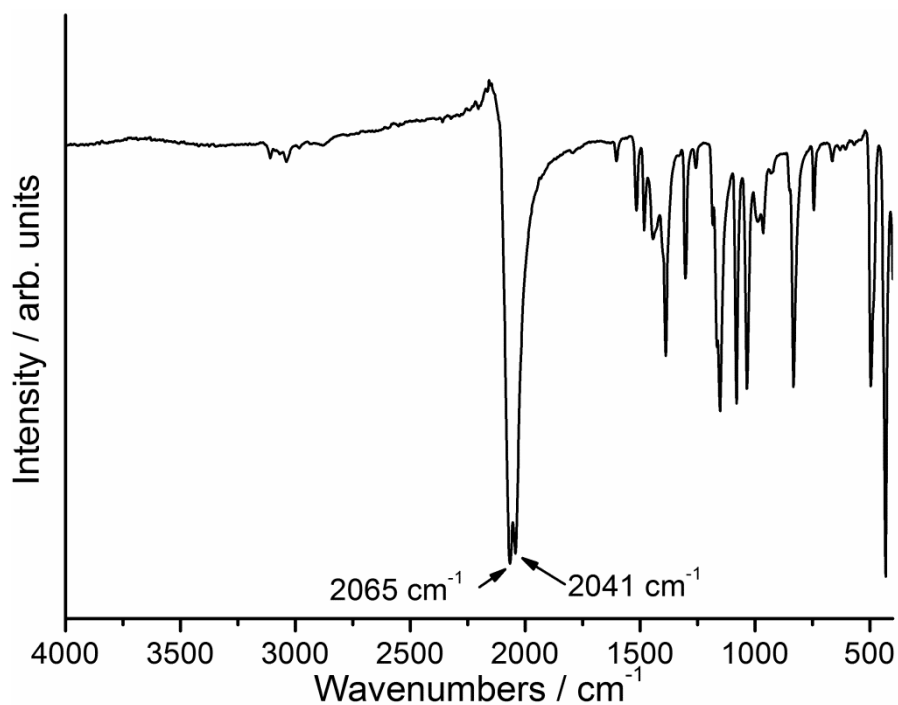


Fig. S13. IR spectrum of the residue, which was obtained in the first heating step of compound **2-Co**.

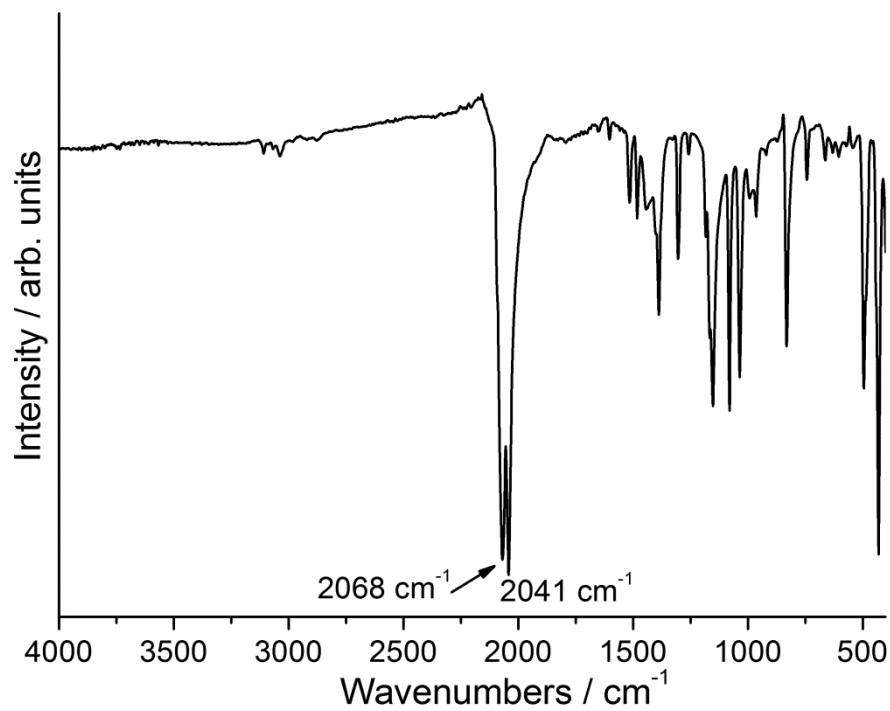


Fig. S14. IR spectrum of the residue, which was obtained in the first heating step of compound **3-Co**.

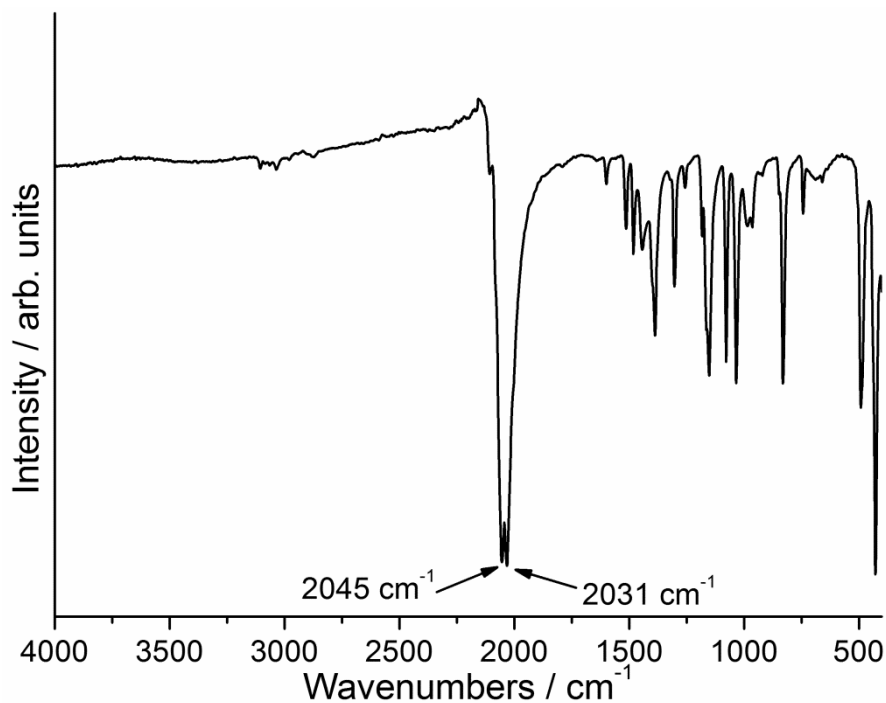


Fig. S15. IR spectrum of the residue, which was obtained in the first heating step of compound **1-Fe**.

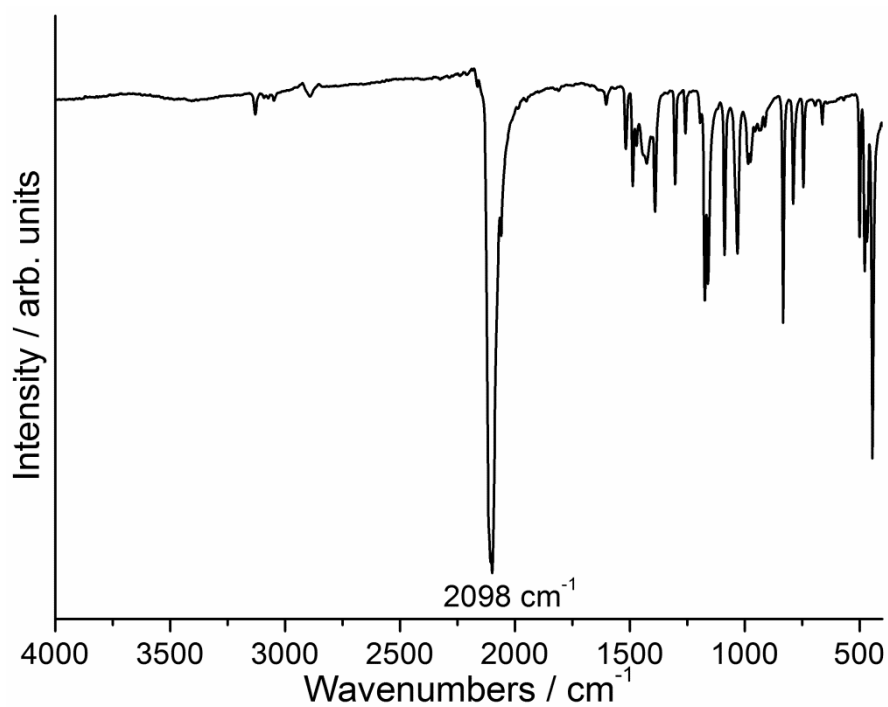


Fig. S16. IR spectrum of the residue, which was obtained in the second heating step of compound **1-Co**.

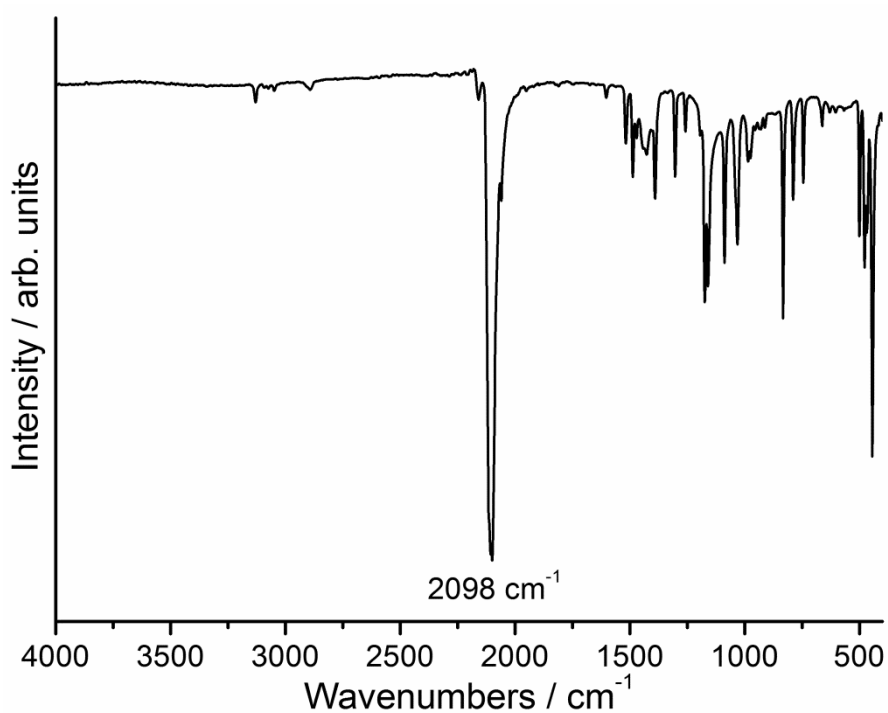


Fig. S17. IR spectrum of the residue, which was obtained in the second heating step of compound **2-Co**.

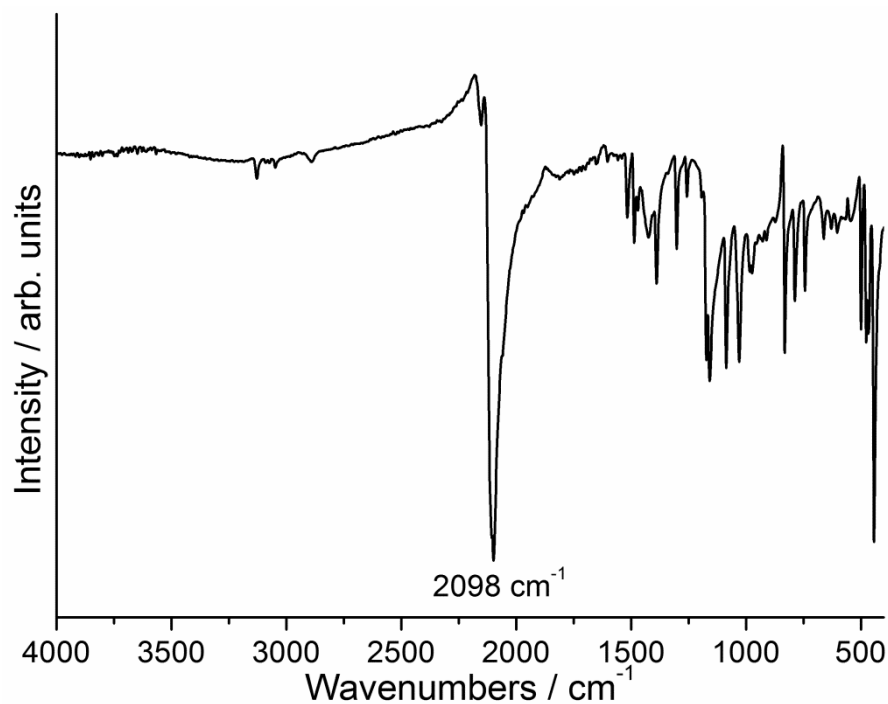


Fig. S18. IR spectrum of the residue, which was obtained in the second heating step of compound **3-Co**.

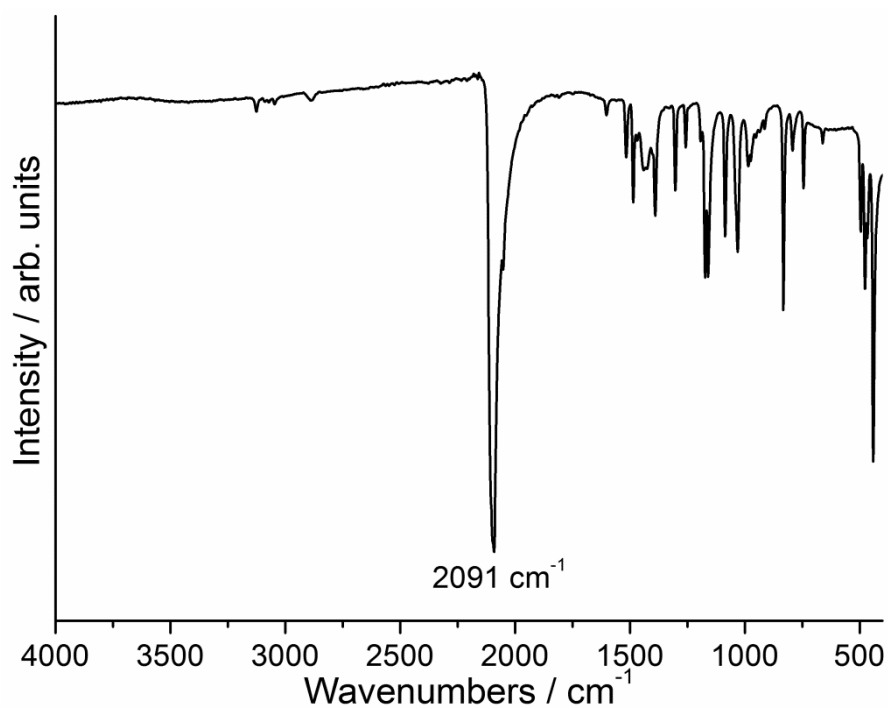


Fig. S19. IR spectrum of the residue, which was obtained in the second heating step of compound **1-Fe**.

Table S3. Selected bond lengths / Å and angles / ° for $[\text{Cd}(\text{NCS})_2(2\text{-methylpyrazine})]_n$ (**5-Cd**). Symmetry transformation used to generate equivalent atoms: A = -x, -y + 2, -z + 1; B = -x + 1/2, y + 1/2, -z + 1/2; C = x - 1/2, -y + 3/2, z - 1/2.

Cd(1)-N(1)	2.2751(19)	Cd(1)-N(11C)	2.4582(17)
Cd(1)-N(2)	2.320(2)	Cd(1)-S(1A)	2.6769(6)
Cd(1)-N(12)	2.4260(18)	Cd(1)-S(2B)	2.6842(6)
N(1)-Cd(1)-N(2)	171.84(8)	N(2)-Cd(1)-S(1A)	84.75(6)
N(1)-Cd(1)-N(12)	86.51(7)	N(12)-Cd(1)-S(1A)	91.75(5)
N(2)-Cd(1)-N(12)	85.60(7)	N(11C)-Cd(1)-S(1A)	90.64(5)
N(1)-Cd(1)-N(11C)	101.36(7)	N(1)-Cd(1)-S(2B)	93.83(5)
N(2)-Cd(1)-N(11C)	86.62(7)	N(2)-Cd(1)-S(2B)	88.03(6)
N(12)-Cd(1)-N(11C)	171.62(6)	N(12)-Cd(1)-S(2B)	88.35(5)
N(1)-Cd(1)-S(1A)	93.41(5)	N(11C)-Cd(1)-S(2B)	88.26(5)
		S(1A)-Cd(1)-S(2B)	172.753(18)

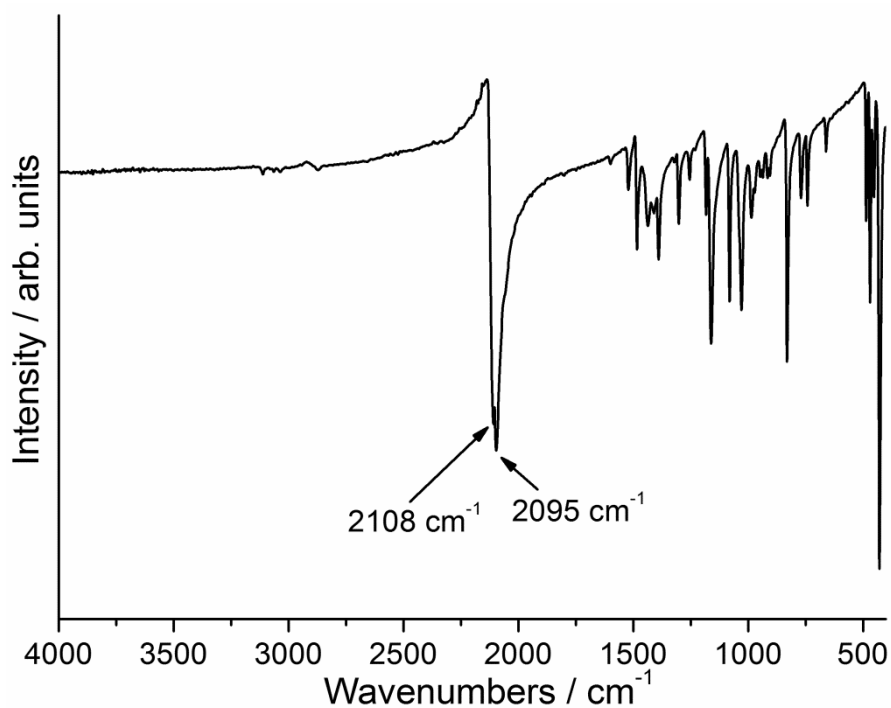


Fig. S20. IR spectrum of compound $[\text{Cd}(\text{NCS})_2(2\text{-methylpyrazine})]_n$ (**5-Cd**).

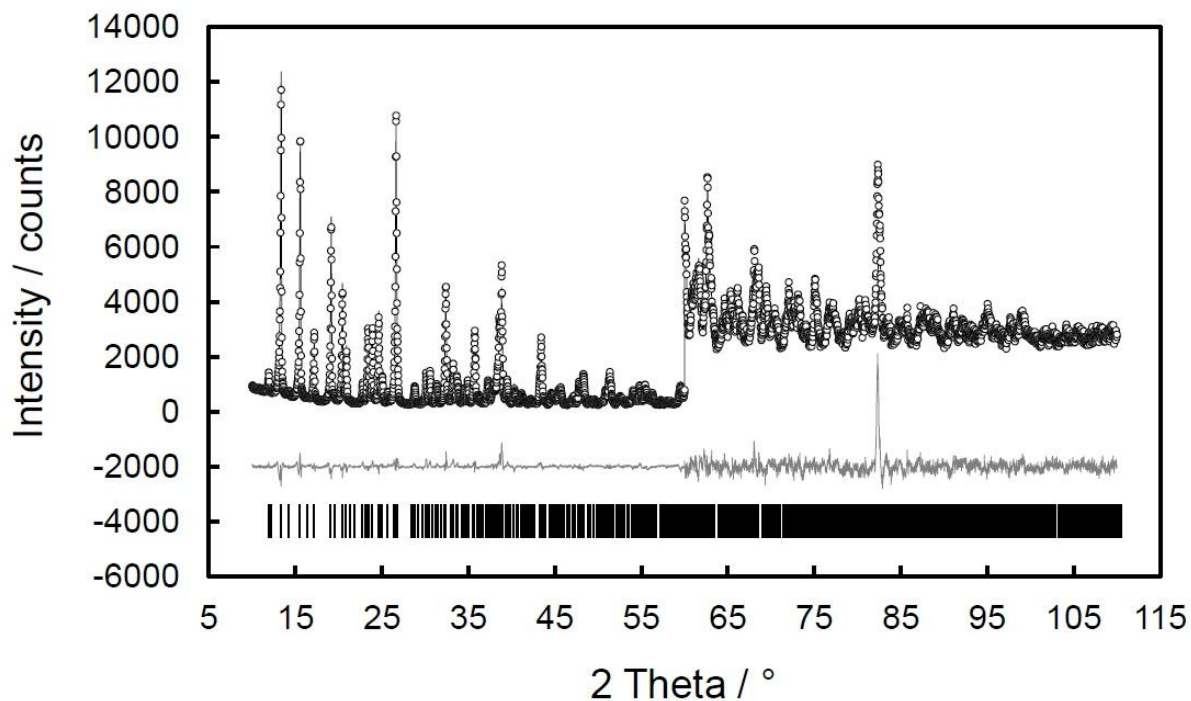


Fig. S21. Difference plot from the Rietveld refinement of $[\text{Co}(\text{NCS})_2(2\text{-methylpyrazine})]_n$ (**5-Co**). Given are observed intensities (circles), calculated intensities (line), the difference (below, arbitrary offset for improved visibility) and the tic-marks for the reflection positions. For the second measurement ($60\text{-}110^\circ$ 2θ), intensities were scaled by a factor 5 for the sake of clarity.

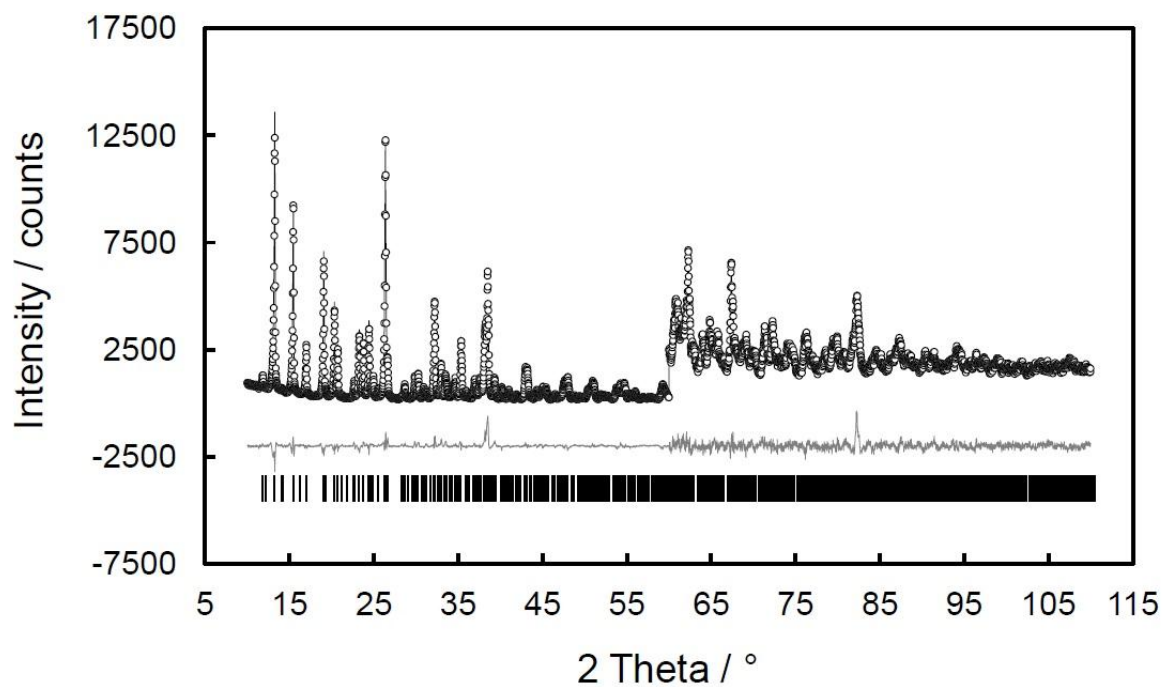


Fig. S22. Difference plot from the Rietveld refinement of $[\text{Fe}(\text{NCS})_2(2\text{-methylpyrazine})]_n$ (**5-Fe**). Given are observed intensities (circles), calculated intensities (line), the difference (below, arbitrary offset for improved visibility) and the tic-marks for the reflection positions. For the second measurement ($60\text{-}110^\circ$ 2θ), intensities were scaled by a factor 5 for the sake of clarity.

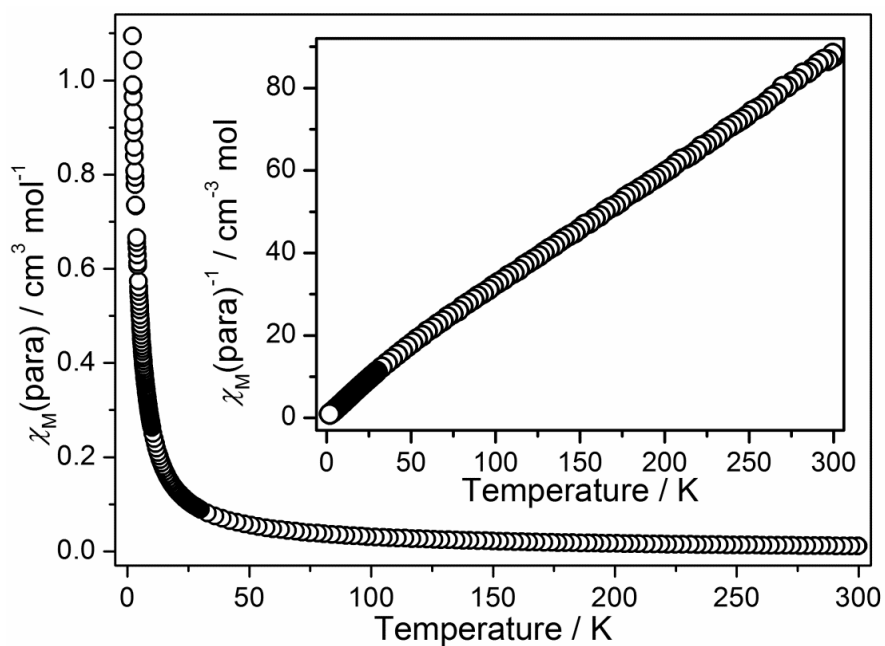


Fig. S23. Molar paramagnetic susceptibility (χ_M) and $1/\chi_M$ (inset) as function of temperature at $H_{\text{DC}} = 1$ kOe for **4-Co**.

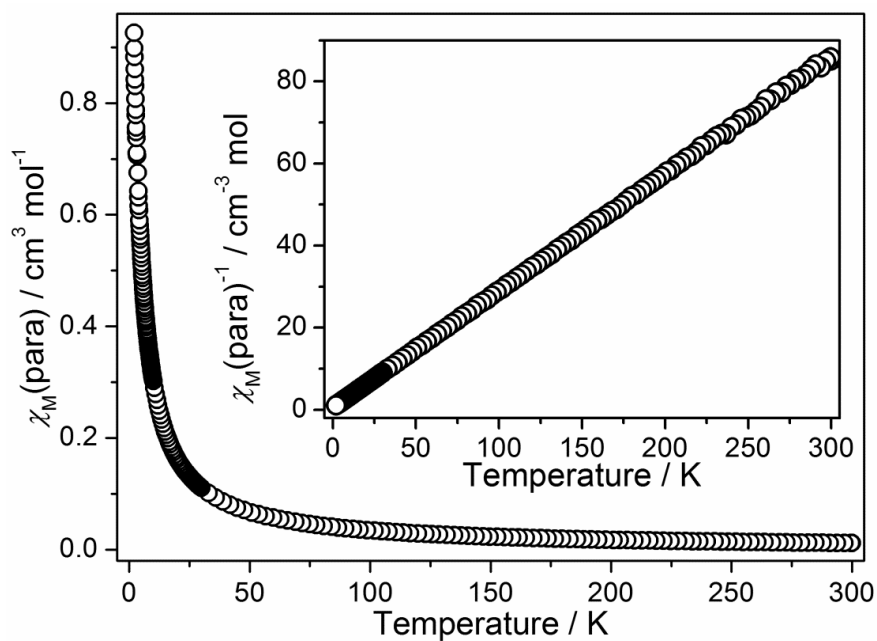


Fig. S24. Molar paramagnetic susceptibility (χ_M) and $1/\chi_M$ (inset) as function of temperature at $H_{\text{DC}} = 1$ kOe for **4-Fe**.

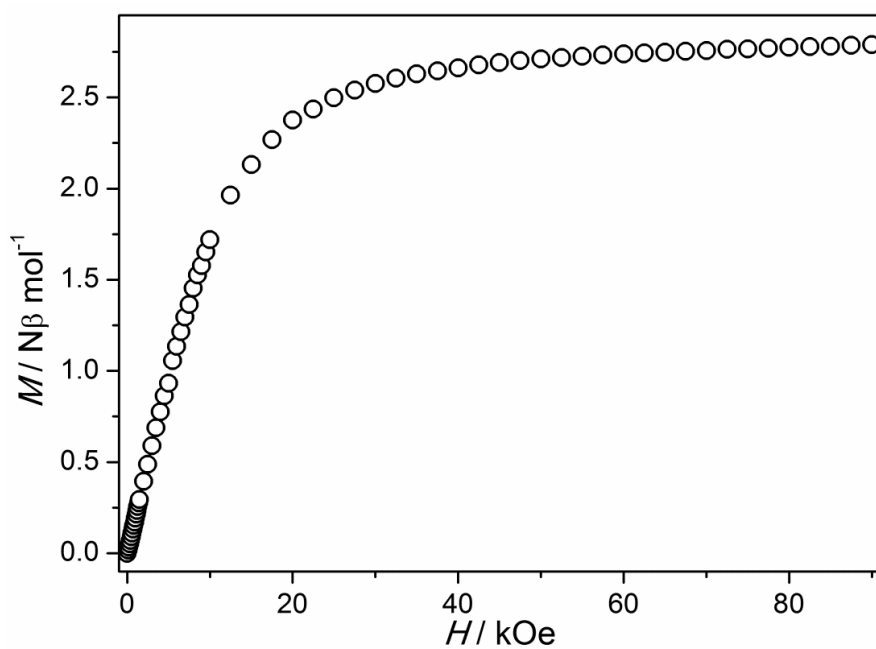


Fig. S25. Initial curve in range of 0 – 90 kOe at $T = 2$ K for **4-Co**.

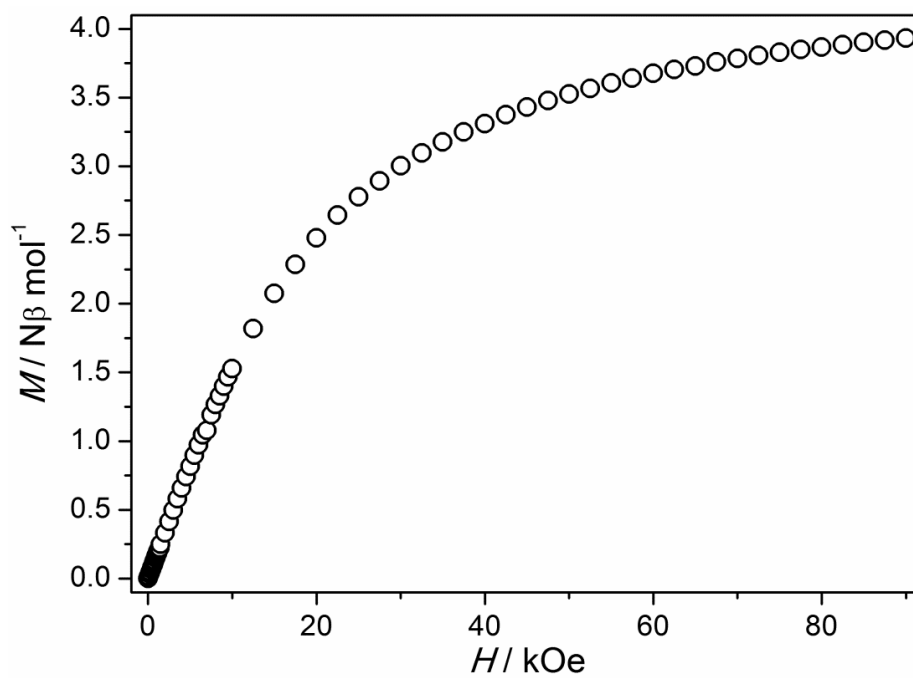


Fig. S26. Initial curve in range of 0 – 90 kOe at $T = 2$ K for **4-Fe**.

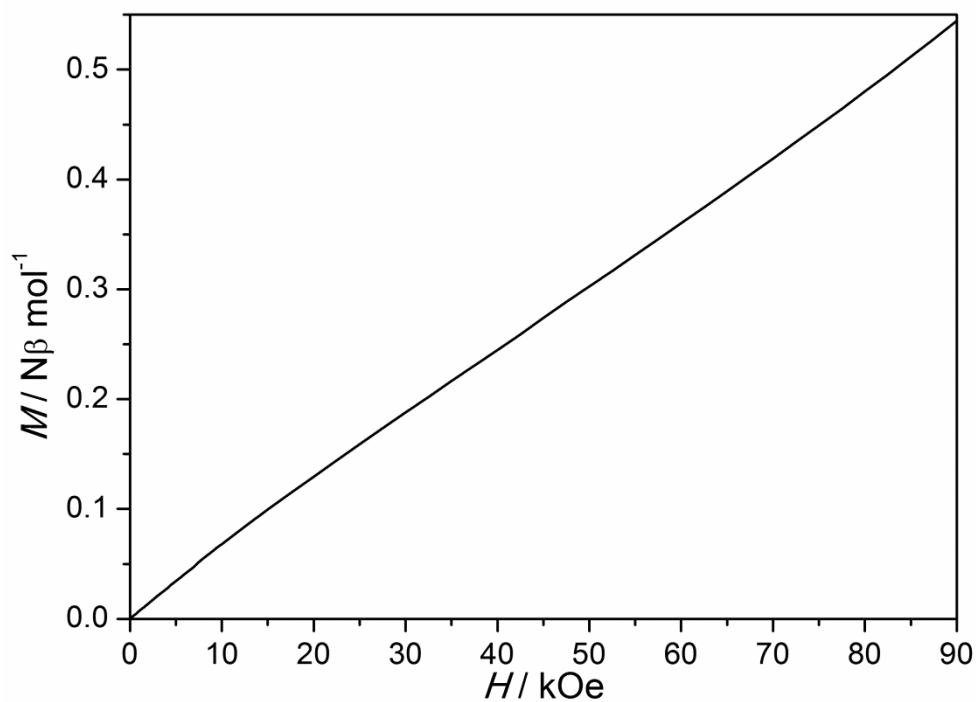


Fig. S27. Initial curve in range of 0 – 90 kOe at $T = 2$ K for **5-Fe**.

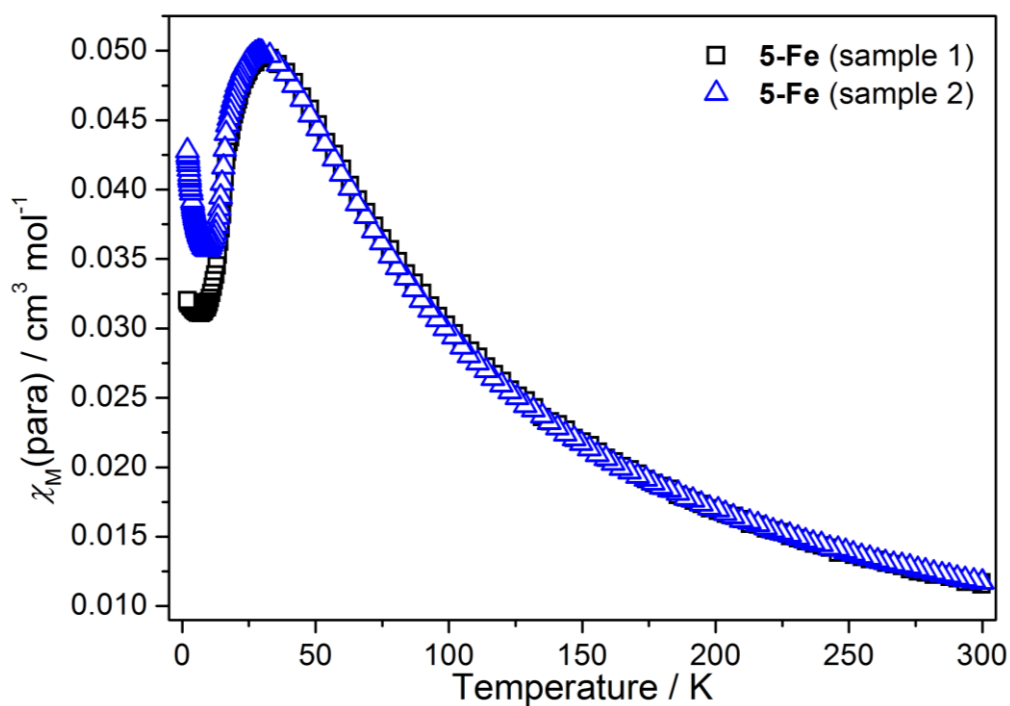


Fig. S28. Molar paramagnetic susceptibility (χ_M) as function of temperature at $H_{\text{DC}} = 1$ kOe for two different batches of **5-Fe**.

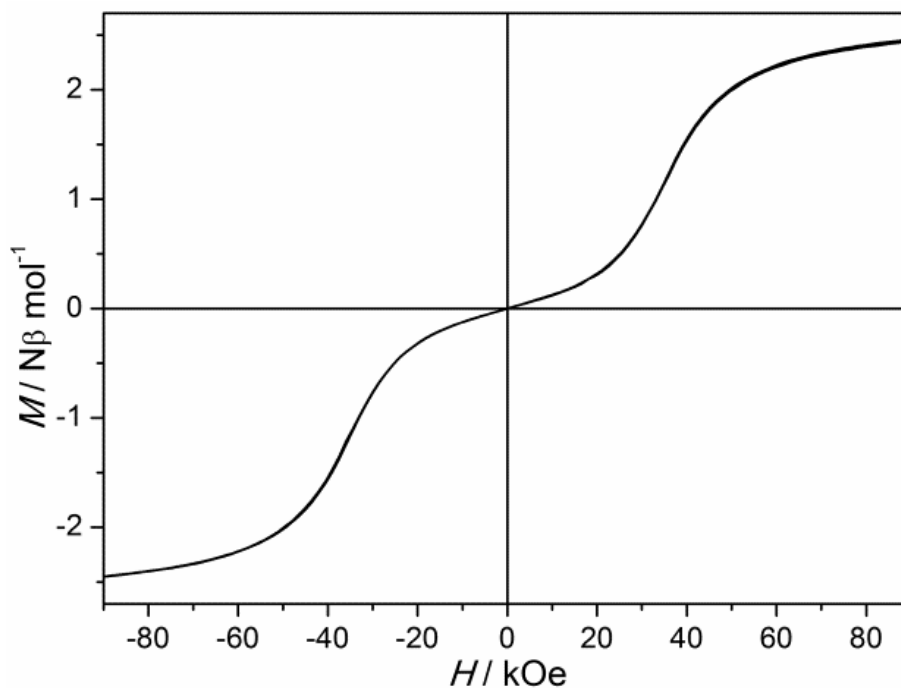


Fig. S29. Saturation magnetization experiment at $T = 2$ K in range of ± 90 kOe for **5-Co**.

Table S4. Results of the magnetic measurements at $H_{\text{DC}} = 40\text{-}90$ kOe for **5-Co**.

$H_{\text{DC}} / \text{kOe}$	40	50	60	70	80	90
$C / \text{cm}^3 \text{K} \cdot \text{mol}^{-1}$	3.54	3.56	3.58	3.58	3.58	3.57
θ / K	-20.5	-20.6	-21.2	-21.4	-21.7	-22.2
$\mu_{\text{eff}}(\text{exp}) / \mu_{\text{B}}$	5.32	5.34	5.35	5.35	5.35	5.35
$\mu_{\text{eff}}(\text{exp}) / \mu_{\text{B}}$	3.87					

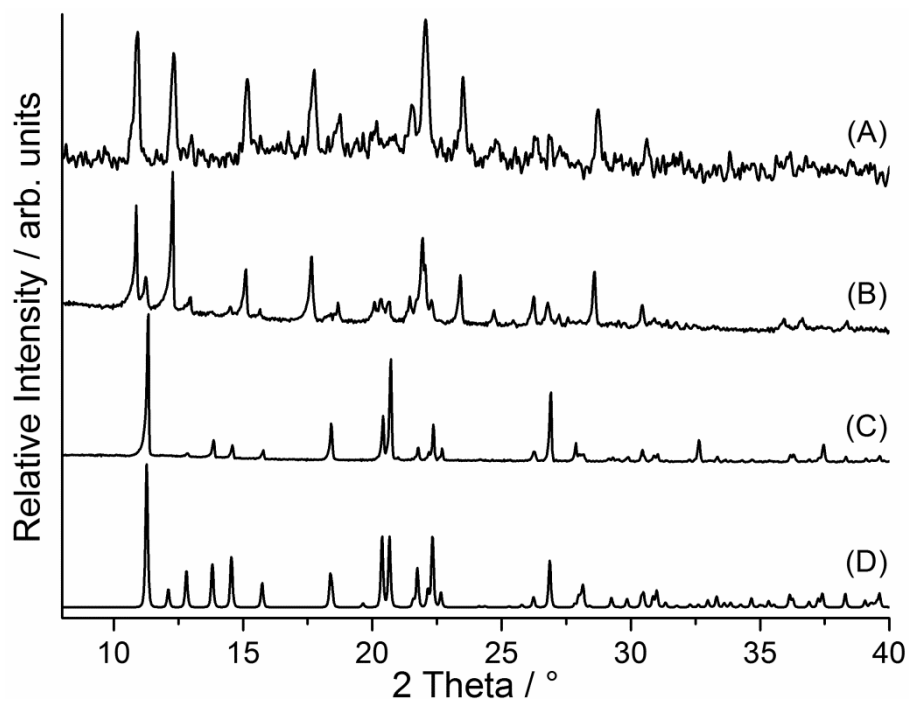


Fig. S30. Experimental XRPD of **2-Co** (A) which were stored for 15 min. (B) and for 1 d in a humid atmosphere (C) together with the calculated powder pattern for **1-Co** (D).