

Supporting Information

Exploration and Synthesis of Condensed Coordination Networks with modified Magnetic Properties

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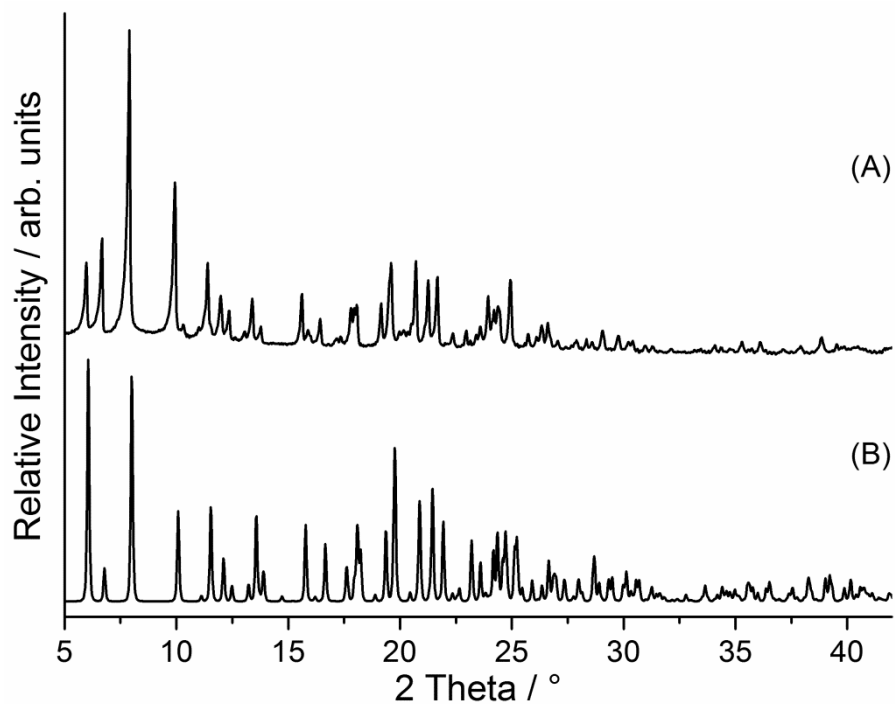


Figure S1. Experimental XRPD of **2** (A) and calculated XRPD from single-crystal data of Ni(NCS)₂(2-methylpyrazine)₄·2-methylpyrazine solvate (**2**) (B).

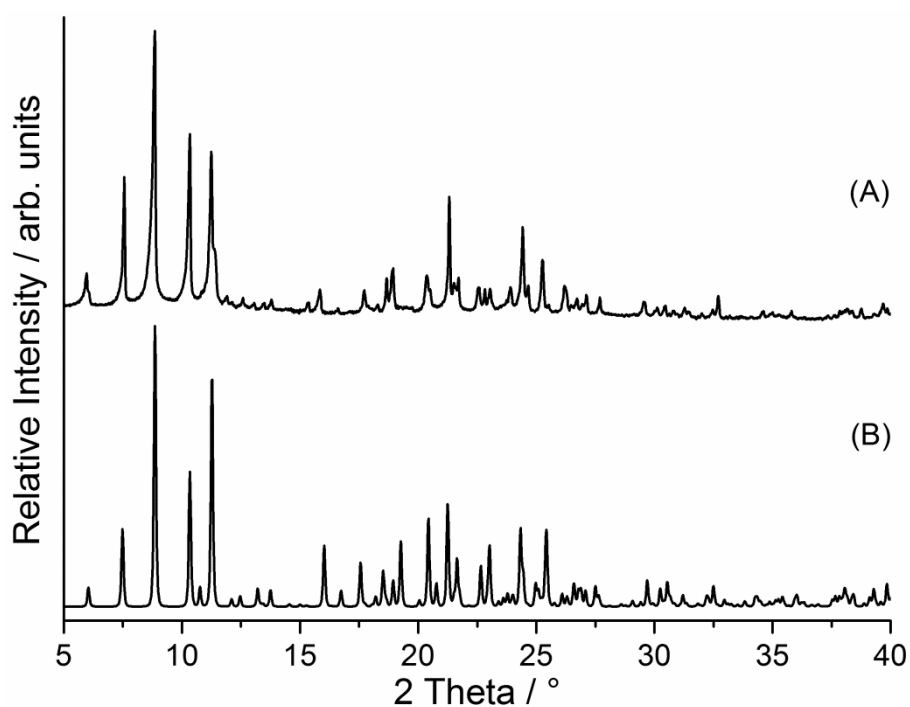


Figure S2. Experimental XRPD of **3** (A) and calculated XRPD from single-crystal data of Ni(NCS)₂(2-methylpyrazine)₄·ethanol solvate (**3**) (B).

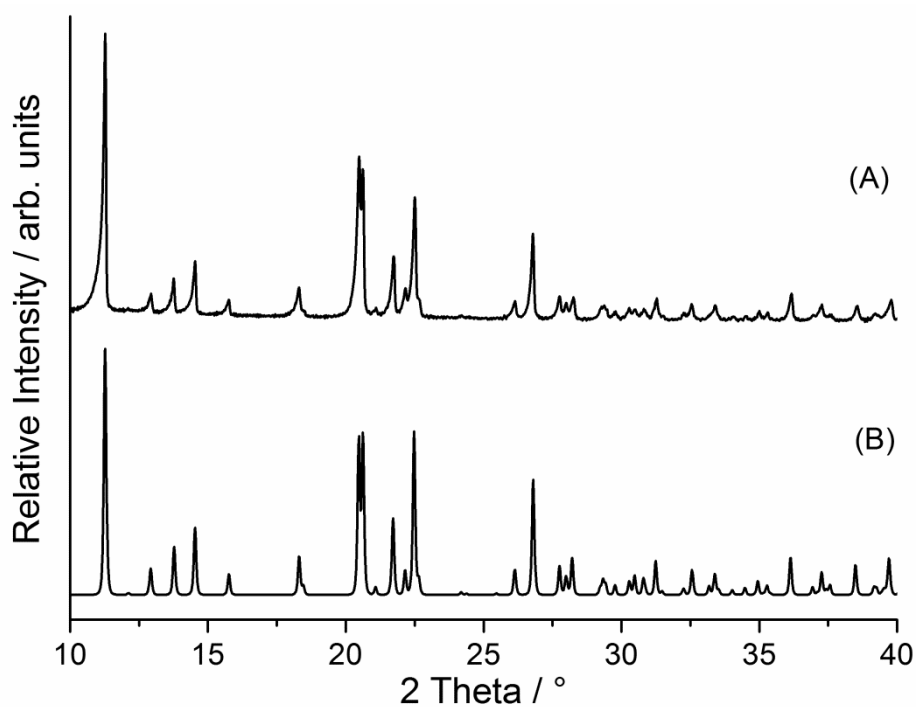


Figure S3. Experimental XRPD of **4** (A) and calculated XRPD for the literature known compound Ni(NCS)₂(2-methylpyrazine)₂(H₂O)₂ (**4**) (B).

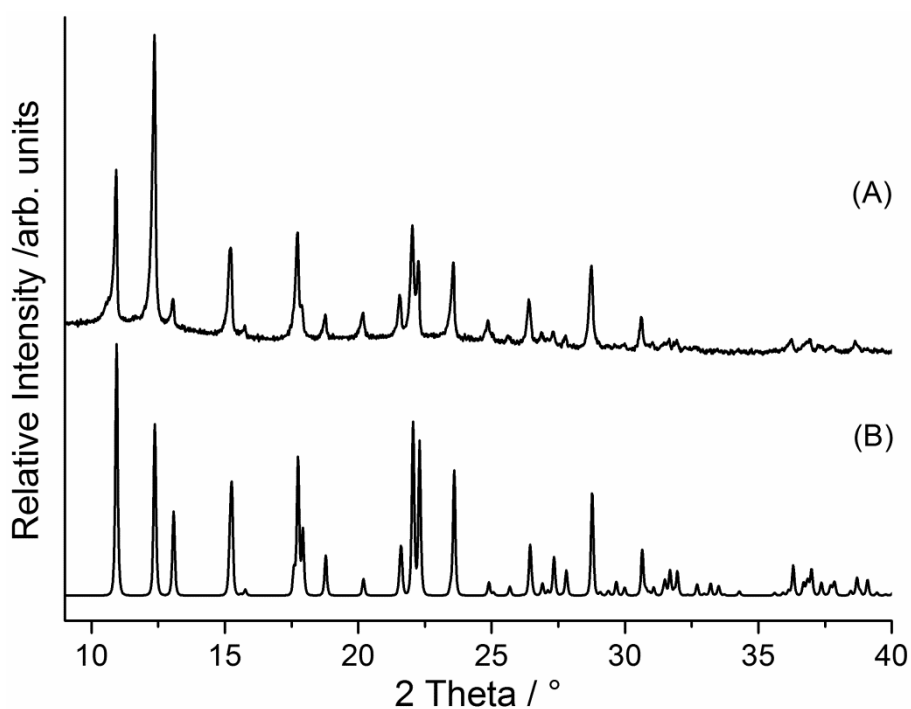


Figure S4. Experimental XRPD of **5** (A) and calculated XRPD from single-crystal data of Ni(NCS)₂(2-methylpyrazine)₂(CH₃OH)₂ (**5**) (B).

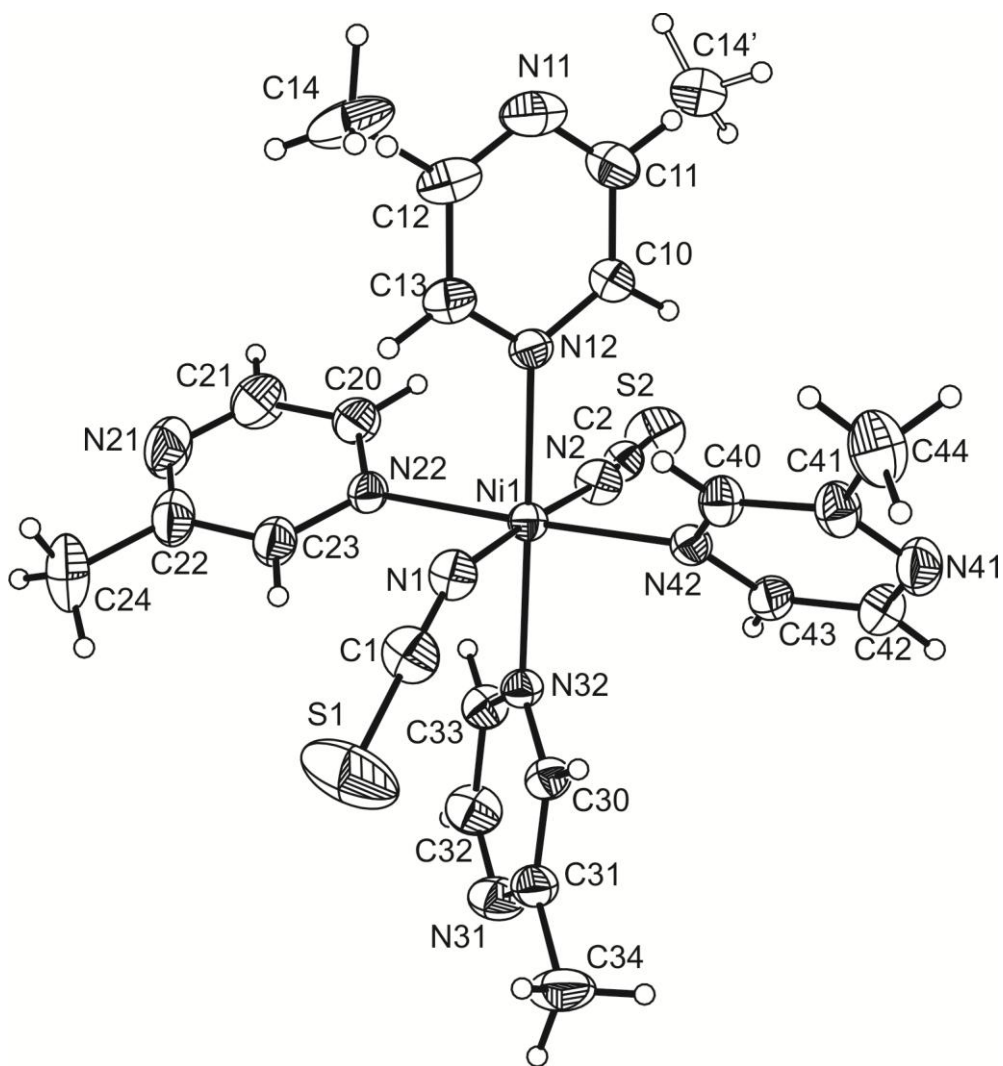


Figure S5. Crystal structure of $\text{Ni}(\text{NCS})_2(2\text{-methylpyrazine})_4$ (**1**) with view of the coordination sphere of the nickel(II) cation with labeling and displacement ellipsoids drawn at 50 % probability level.

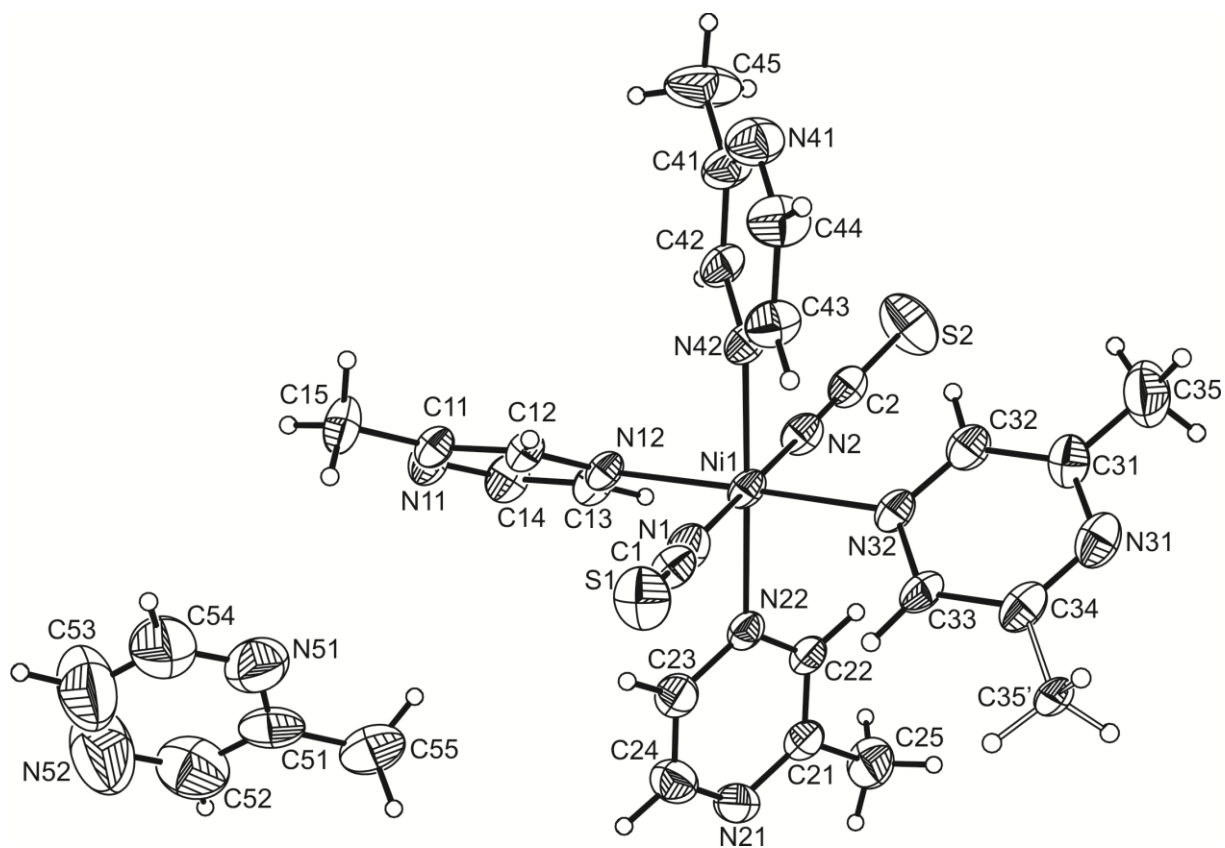


Figure S6. Crystal structure of $\text{Ni}(\text{NCS})_2(2\text{-methylpyrazine})_4 \cdot 2\text{-methylpyrazine}$ solvate (**2**) with view of the coordination sphere of the nickel(II) cation with labeling and displacement ellipsoids drawn at 50 % probability level.

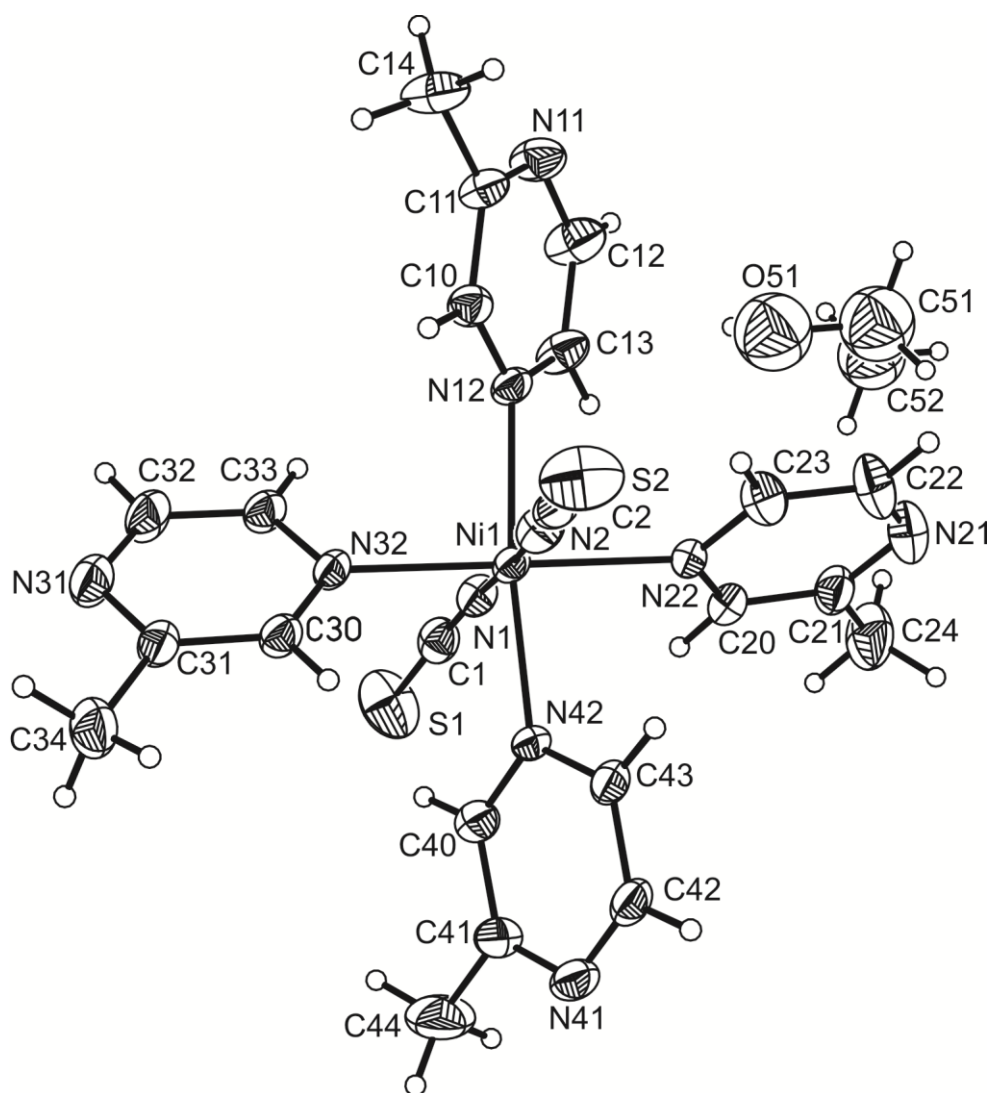


Figure S7. Crystal structure of $\text{Ni}(\text{NCS})_2(2\text{-methylpyrazine})_4\text{-ethanol solvate (3)}$ with view of the coordination sphere of the nickel(II) cation with labeling and displacement ellipsoids drawn at 50 % probability level.

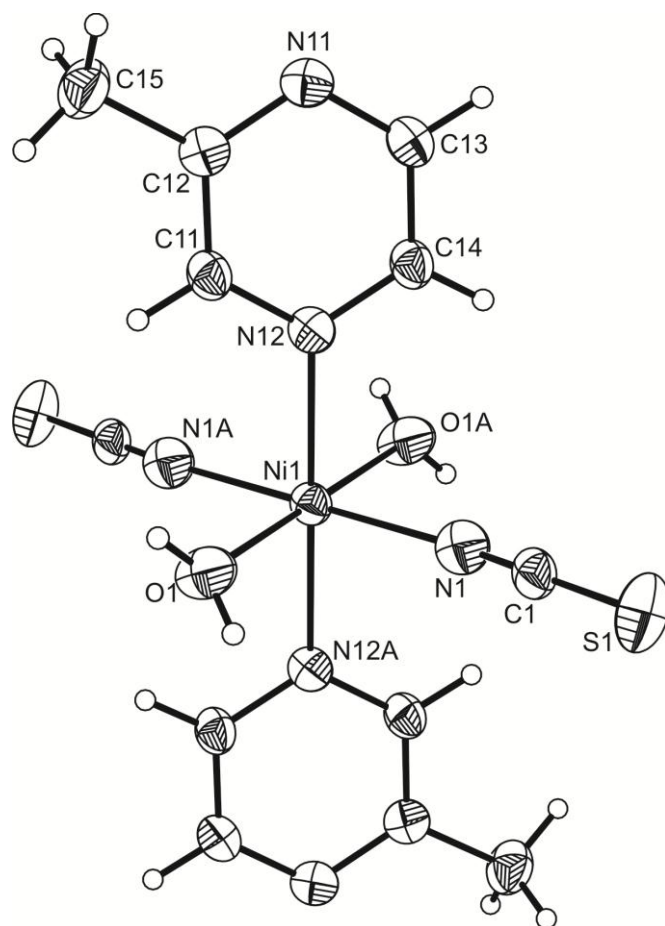


Figure S8. Crystal structure of $\text{Ni}(\text{NCS})_2(2\text{-methylpyrazine})_2(\text{H}_2\text{O})_2$ (**4**) with view of the coordination sphere of the nickel(II) cation with labeling and displacement ellipsoids drawn at 50 % probability level. Symmetry code: A = -x, -y, -z + 1.

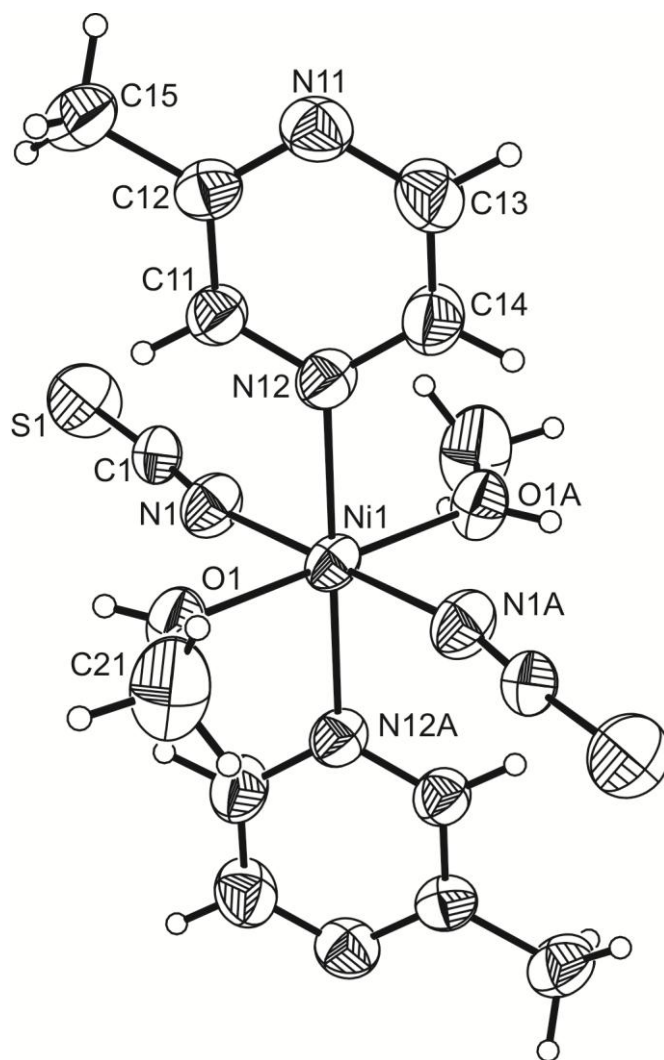


Figure S9. Crystal structure of Ni(NCS)₂(2-methylpyrazine)₂(CH₃OH)₂ (**5**) with view of the coordination sphere of the nickel(II) cation with labeling and displacement ellipsoids drawn at 50 % probability level. Symmetry code: A = -x + 1, -y + 1, -z.

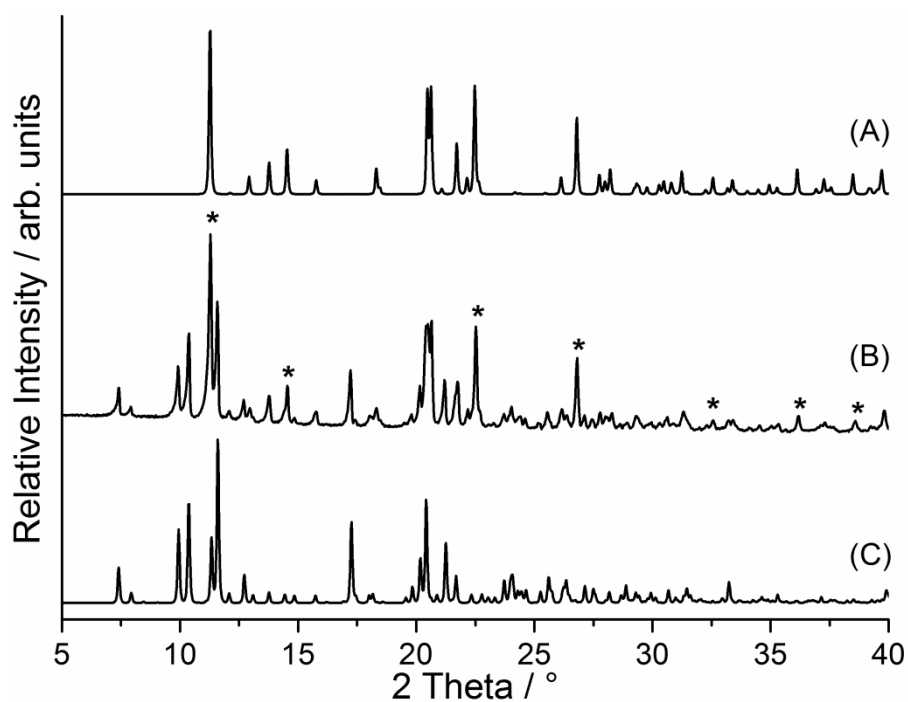


Figure S10. Experimental XRPD of **6** (B) (the reflections of the 1:2:2 compound Ni(NCS)₂(2-methylpyrazine)₂(H₂O)₂ (**4**) are indicated by stars) and calculated XRPD from single-crystal data of [Ni(NCS)₂(2-methylpyrazine)₄·Ni(NCS)₂(2-methylpyrazine)₃(H₂O)] (**6**; C) together with the calculated XRPD from single-crystal data of Ni(NCS)₂(2-methylpyrazine)₂(H₂O)₂ (**4**; A).

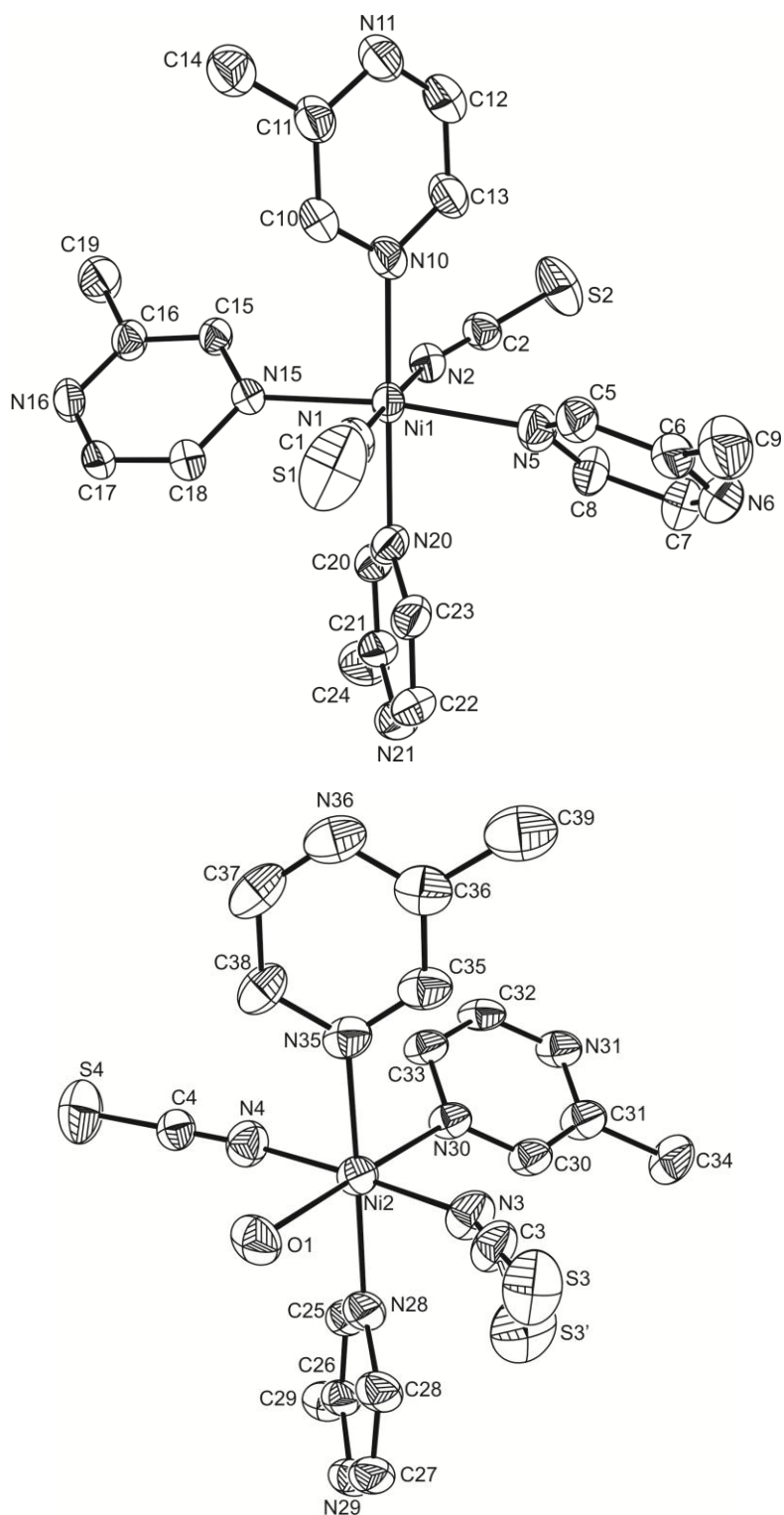


Figure S11. Crystal structure of $[\text{Ni}(\text{NCS})_2(2\text{-methylpyrazine})_4]\cdot\text{Ni}(\text{NCS})_2(2\text{-methylpyrazine})_3(\text{H}_2\text{O})$ (**6**) with view of the coordination sphere of the nickel(II) cation with labeling and displacement ellipsoids drawn at 50 % probability level. The hydrogen atoms were omitted for clarity.

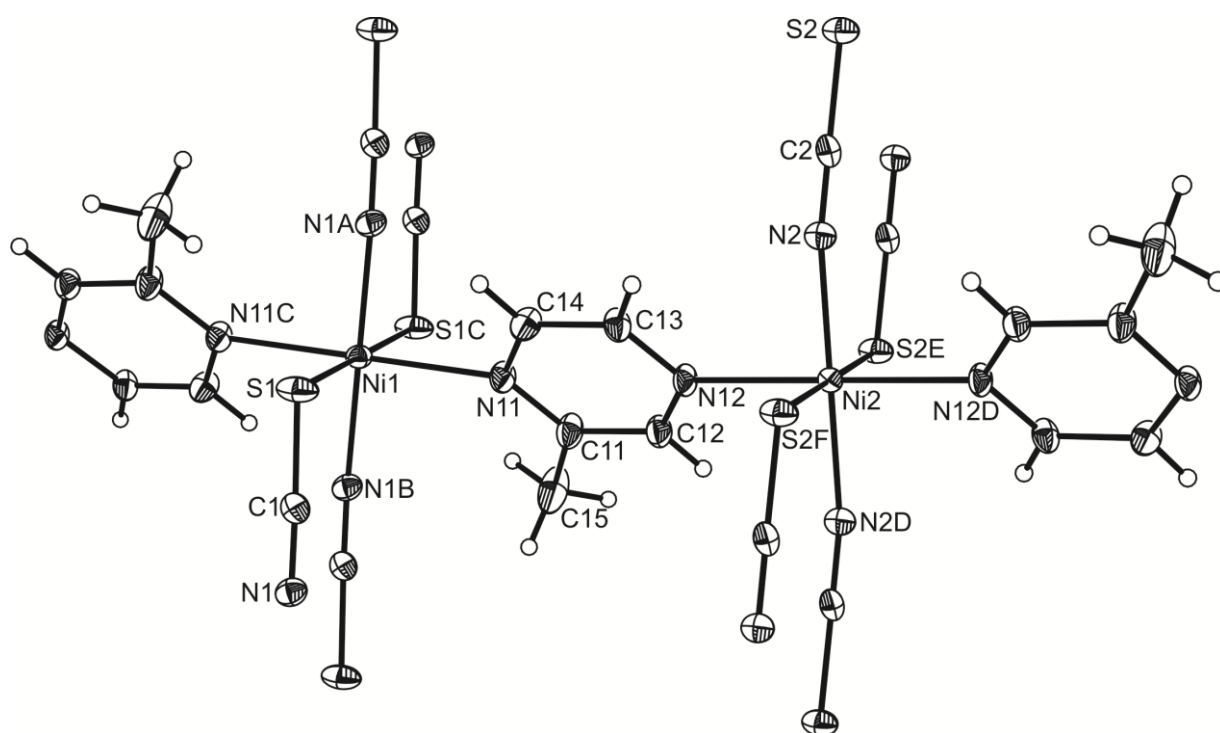


Figure S12. Crystal structure of $[\text{Ni}(\text{NCS})_2(2\text{-methylpyrazine})]_n$ (**8**) with view of the coordination sphere of the nickel(II) cation with labeling and displacement ellipsoids drawn at 50 % probability level. Symmetry codes: A = $x, y - 1, z$; B = $-x, -y + 2, -z + 1$; C = $-x, -y + 1, -z + 1$; D = $-x + 1, -y + 1, -z + 1$; E = $-x + 1, -y, -z + 1$; F = $x, y + 1, z$.

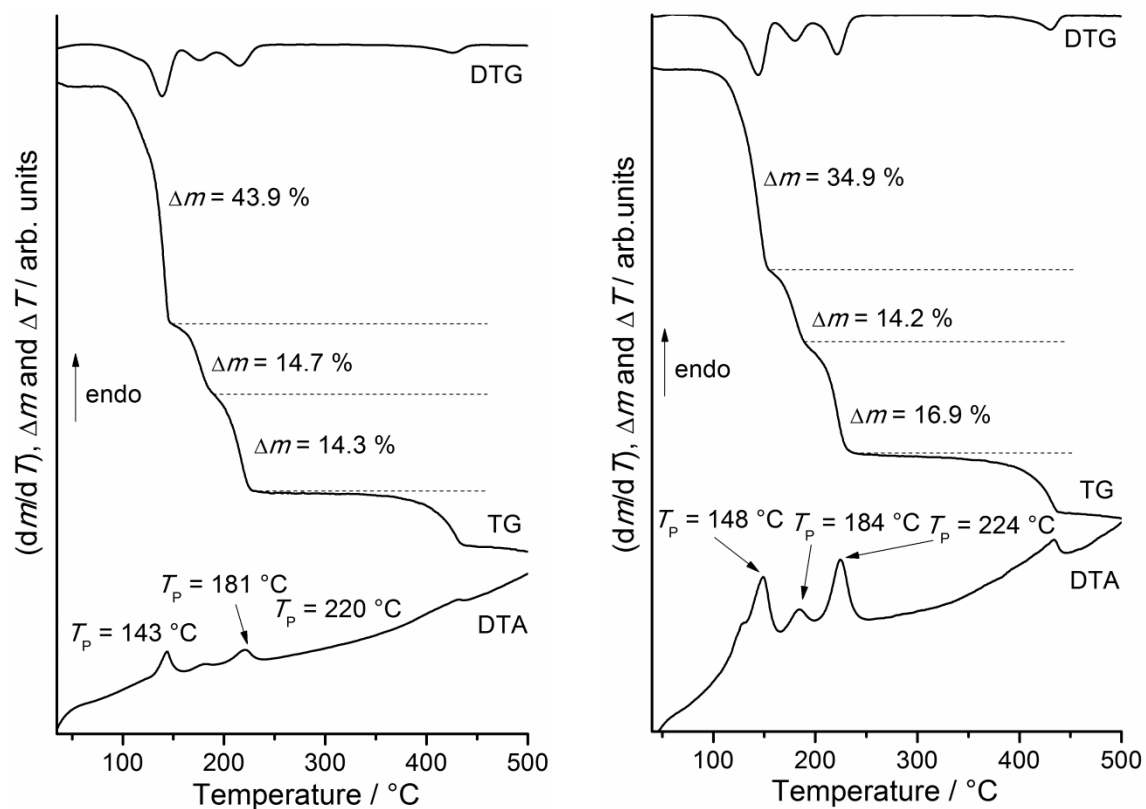


Figure S13. DTA, DTG and TG curves of the ligand-rich 1:5 compounds Ni(NCS)₂(2-methylpyrazine)₄·2-methylpyrazine solvate (**2**) (left) and Ni(NCS)₂(2-methylpyrazine)₄·ethanol solvate (**3**) (right). Heating rate = 4°C/min; given are the peak temperatures T_p in °C and the mass loss in %.

Table S1. Experimental and calculated mass losses of the ligand-rich 1:5 compounds: Ni(NCS)₂(2-methylpyrazine)₄·2-methylpyrazine solvate (**2**) and Ni(NCS)₂(2-methylpyrazine)₄·ethanol solvate (**3**).

	2		3
Δm_{exp} (1. step)	43.9	Δm_{exp} (1. step)	34.9
Δm_{calc} (-3x2-methylpyrazine)	43.8	Δm_{calc} (-2x2-methylpyrazine)	31.50
Δm_{exp} (2. step)	14.7	Δm_{exp} (2. step)	14.2
Δm_{calc} (-1x2-methylpyrazine)	14.6	Δm_{calc} (-1x2-methylpyrazine)	15.7
Δm_{exp} (3. step)	14.3	Δm_{exp} (3. step)	16.9
Δm_{calc} (-1x2-methylpyrazine)	14.6	Δm_{calc} (-1x2-methylpyrazine)	15.7

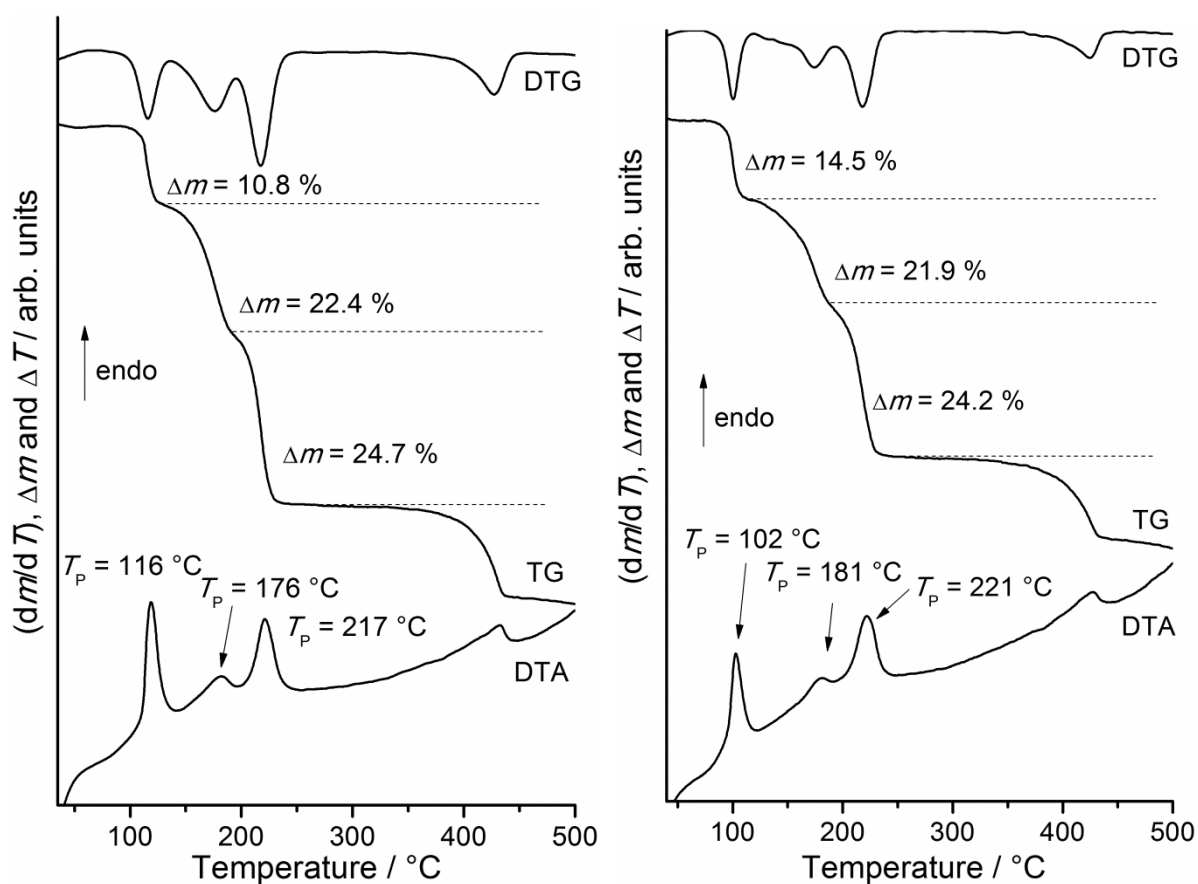


Figure S14. DTA, DTG and TG curves of the ligand-rich 1:2:2 compounds Ni(NCS)₂(2-methylpyrazine)₂(H₂O)₂ (**4**) (left) and Ni(NCS)₂(2-methylpyrazine)₂(CH₃OH)₂ (**5**) (right). Heating rate = 4 °C/min; given are the peak temperatures T_P in °C and the mass loss in %.

Table S2. Experimental and calculated mass losses of the ligand-rich 1:2:2 compounds: Ni(NCS)₂(2-methylpyrazine)₂(H₂O)₂ (**4**) and Ni(NCS)₂(2-methylpyrazine)₂(CH₃OH)₂ (**5**).

	4		5
Δm_{exp} (1. step)	10.8	Δm_{exp} (1. step)	14.5
Δm_{calc} (-2 H ₂ O)	9.01	Δm_{calc} (-2 CH ₃ OH)	14.9
Δm_{exp} (2. step)	22.4	Δm_{exp} (2. step)	21.9
Δm_{calc} (-1x2-methylpyrazine)	23.5	Δm_{calc} (-1x2-methylpyrazine)	23.5
Δm_{exp} (3. step)	24.7	Δm_{exp} (3. step)	24.2
Δm_{calc} (-1x2-methylpyrazine)	23.5	Δm_{calc} (-1x2-methylpyrazine)	23.5

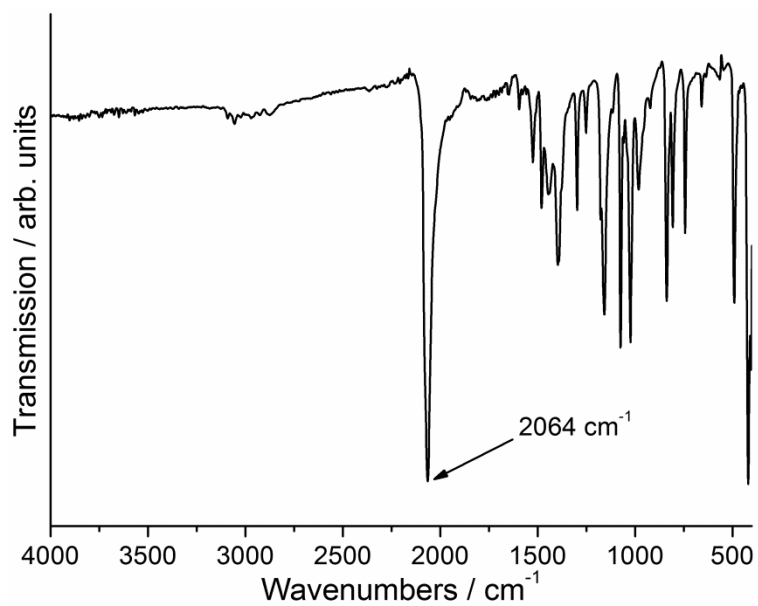


Figure S15. IR spectrum of the ligand-rich compound $\text{Ni}(\text{NCS})_2(2\text{-methylpyrazine})_4 \cdot 2\text{-methylpyrazine}$ solvate (**2**).

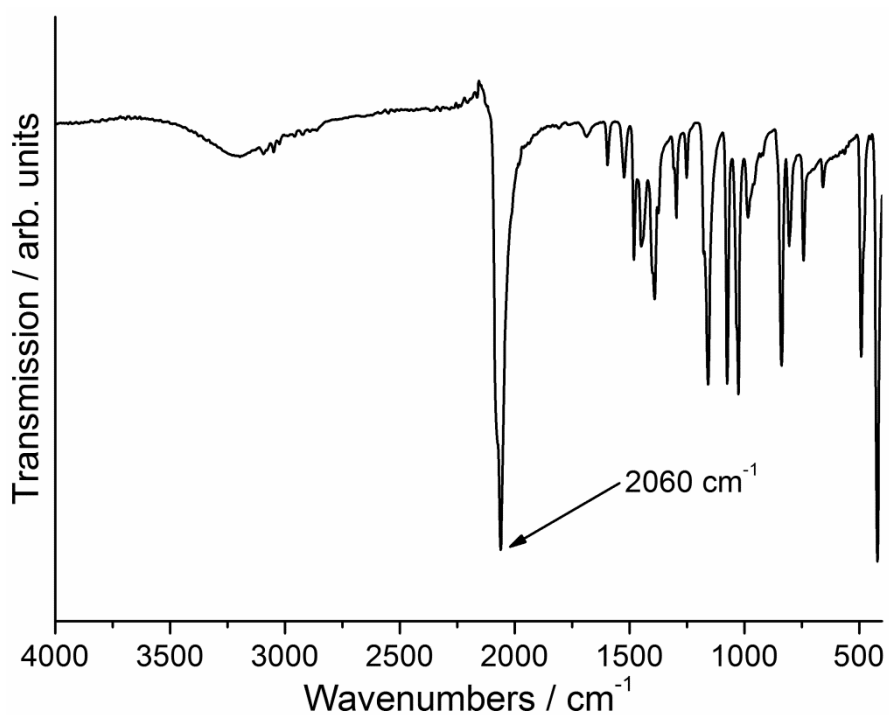


Figure S16. IR spectrum of the ligand-rich compound $\text{Ni}(\text{NCS})_2(2\text{-methylpyrazine})_4 \cdot \text{ethanol}$ solvate (**3**).

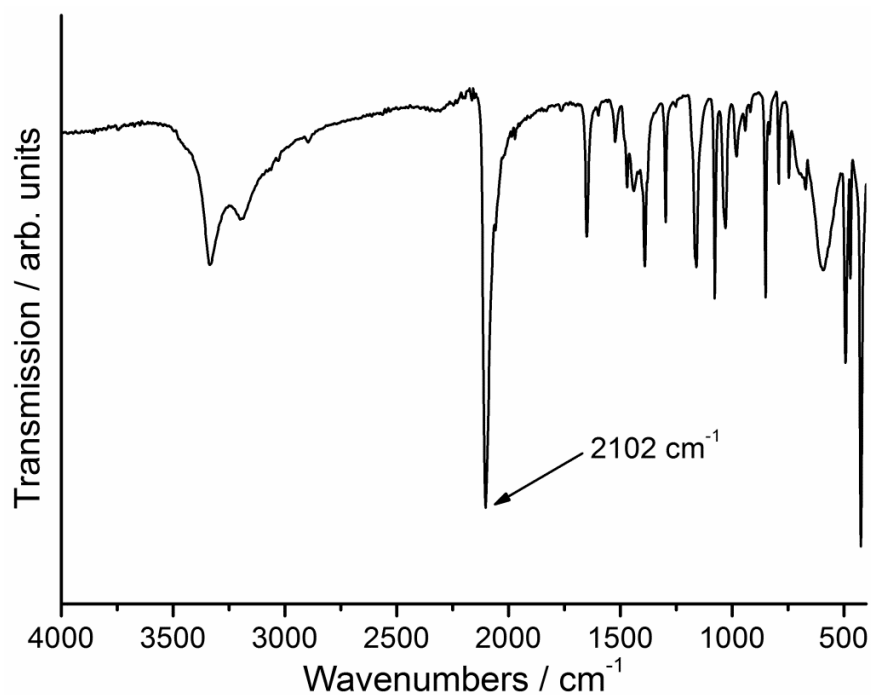


Figure S17. IR spectrum of the ligand-rich 1:2:2 compound $\text{Ni}(\text{NCS})_2(2\text{-methylpyrazine})_2(\text{H}_2\text{O})_2$ (**4**).

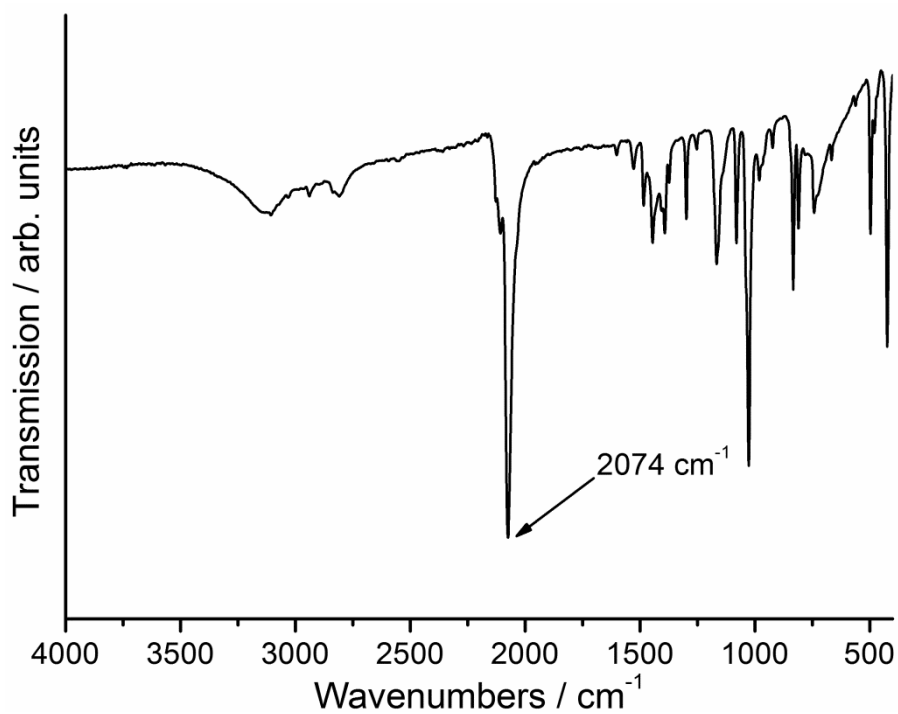


Figure S18. IR spectrum of the ligand-rich 1:2:2 compound $\text{Ni}(\text{NCS})_2(2\text{-methylpyrazine})_2(\text{CH}_3\text{OH})_2$ (**5**).

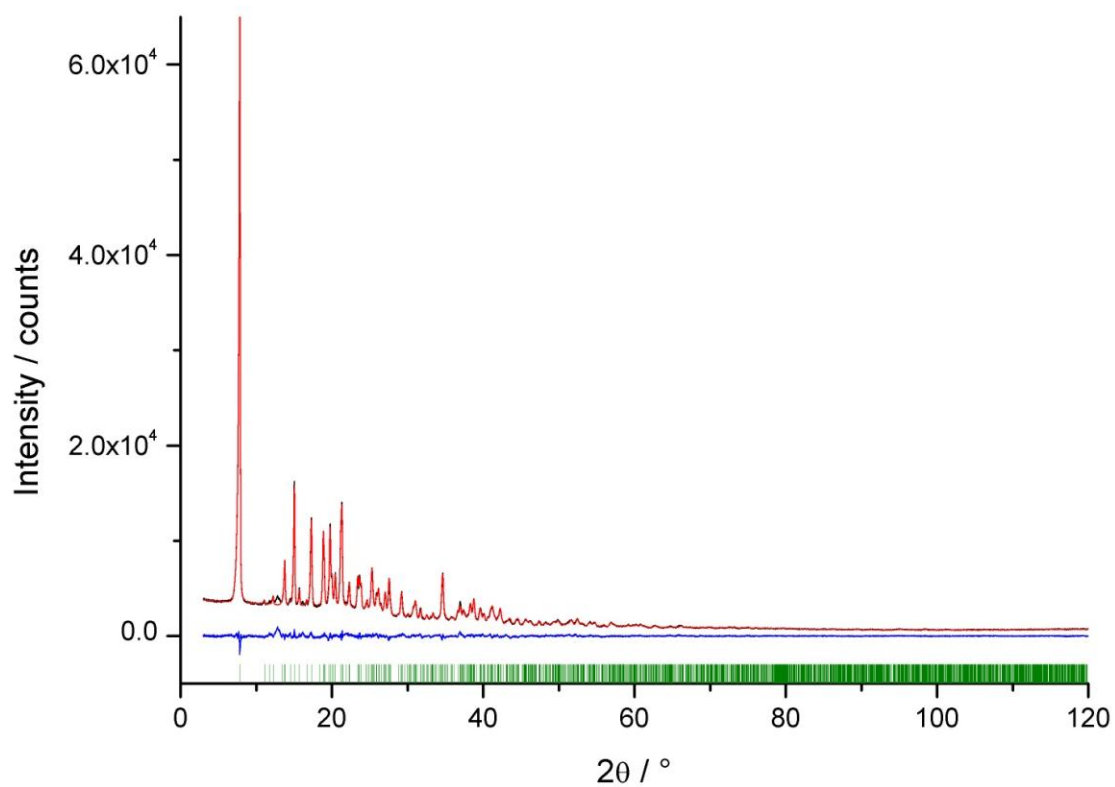


Figure S19. Difference plot of the Rietveld refinement of compound $[\text{Ni}(\text{NCS})_2(2\text{-methylpyrazine})_2]_n$ (**7**).

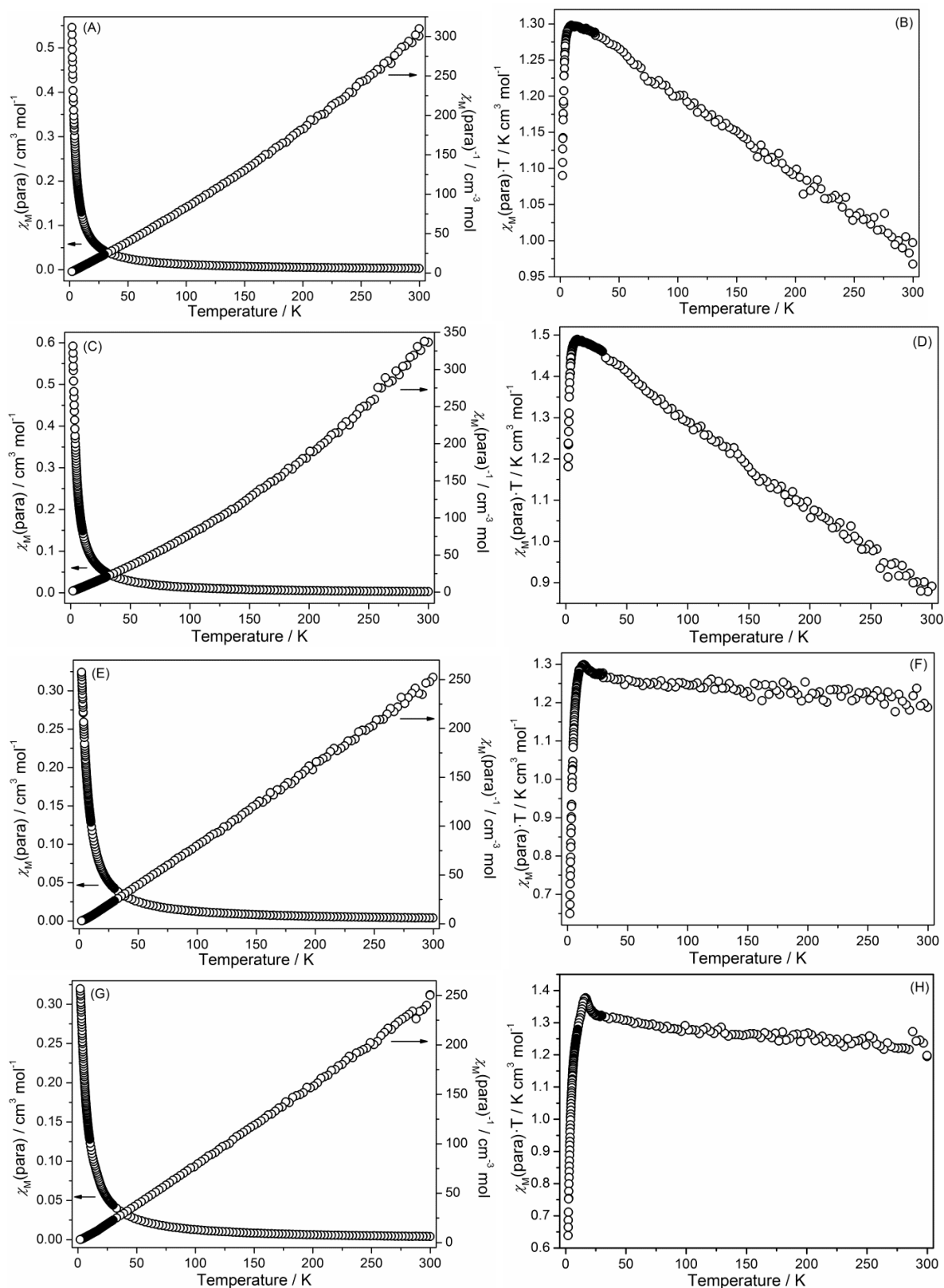


Figure S20. Plots of paramagnetic susceptibility and reciprocal paramagnetic susceptibility (A, C, E, G) and $\chi_M T$ (B, D, F, H) as function of temperature for the 2-methylpyrazine-rich compounds $\text{Ni}(\text{NCS})_2(2\text{-methylpyrazine})_4 \cdot 2\text{-methylpyrazine}$ solvate (**2**) (A, B), $[\text{Ni}(\text{NCS})_2(2\text{-methylpyrazine})_4 \cdot \text{ethanol}]$ solvate (**3**) (C, D), $\text{Ni}(\text{NCS})_2(2\text{-methylpyrazine})_2(\text{H}_2\text{O})_2$ (**4**) and $\text{Ni}(\text{NCS})_2(2\text{-methylpyrazine})_2(\text{CH}_3\text{OH})_2$ (**5**) (E, F) and (G, H).

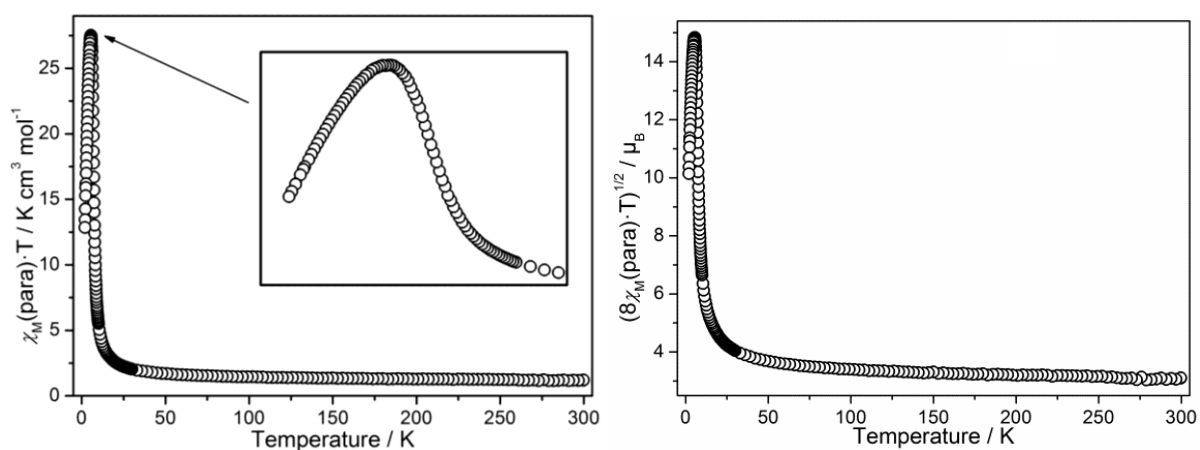


Figure S21. Results of the magnetic measurements for **7**: and $\sqrt{8(\chi T)}$ (left) and χT (right) as function of temperature (at $H_{\text{DC}} = 1$ kOe).

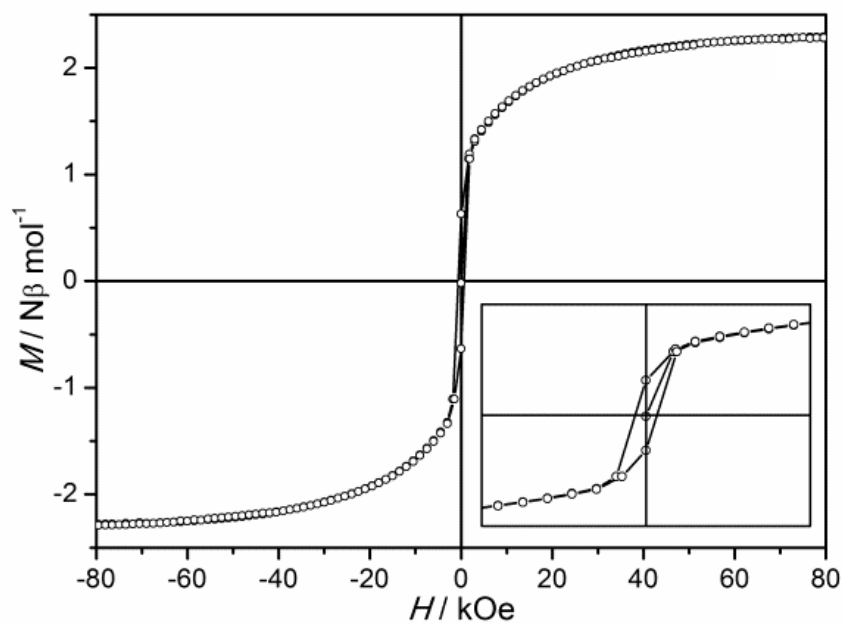


Figure S22. Magnetization experiment at $T = 2$ K in range of $H = \pm 90$ kOe.

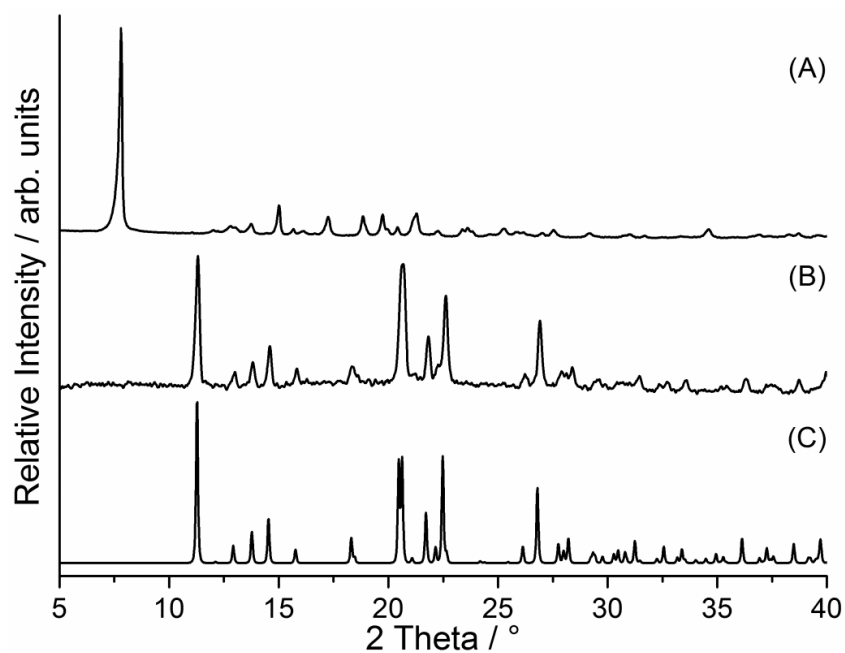


Figure S23. Experimental XRPD of **7** (A) obtained in the first TG step of the thermal decomposition reaction of **4**, which was stored for 1 d in a saturated water atmosphere (B) together with the calculated XRPD of compound $\text{Ni}(\text{NCS})_2(2\text{-methylpyrazine})_2(\text{H}_2\text{O})_2$ (C).

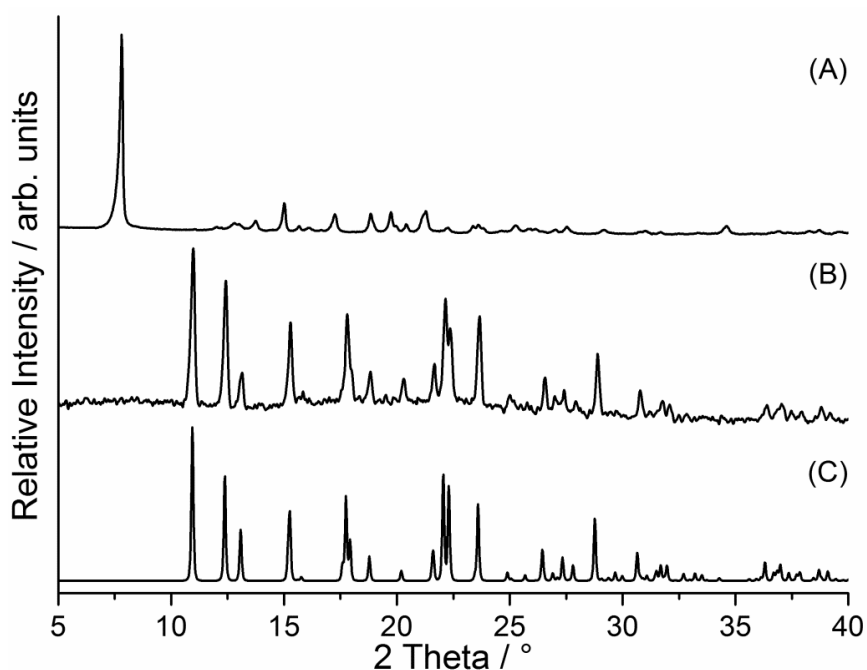


Figure S24. Experimental XRPD of **7** (A) obtained in the first TG step of the thermal decomposition reaction of **5**, which was stored for 1 d in a saturated methanol atmosphere (B) together with the calculated XRPD of compound $\text{Ni}(\text{NCS})_2(2\text{-methylpyrazine})_2(\text{CH}_3\text{OH})_2$ (C).

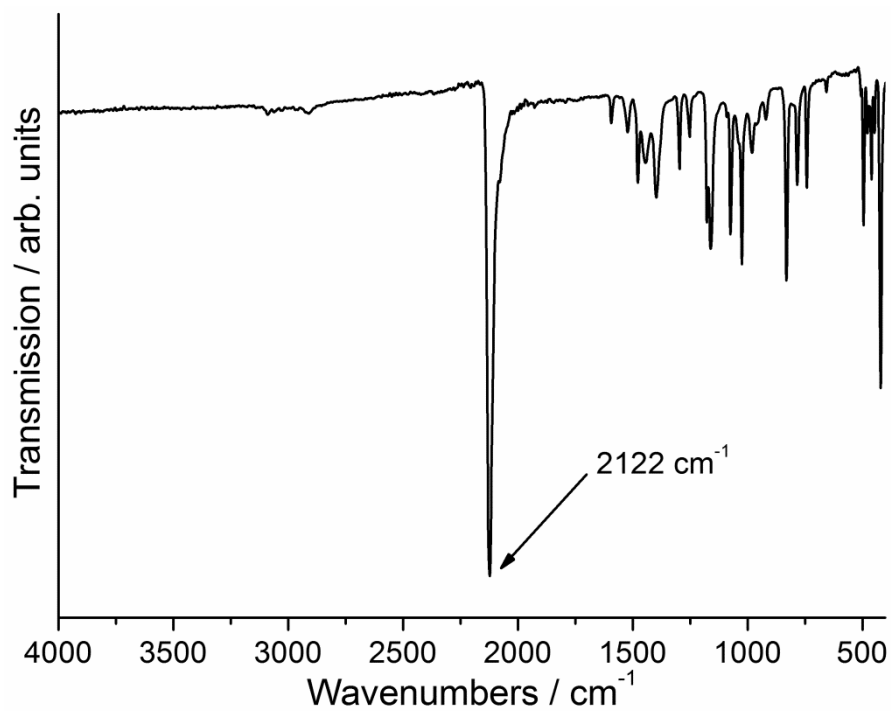


Figure S25. IR spectrum of the residue obtained after the first TG step of the thermal decomposition reaction of **2**.

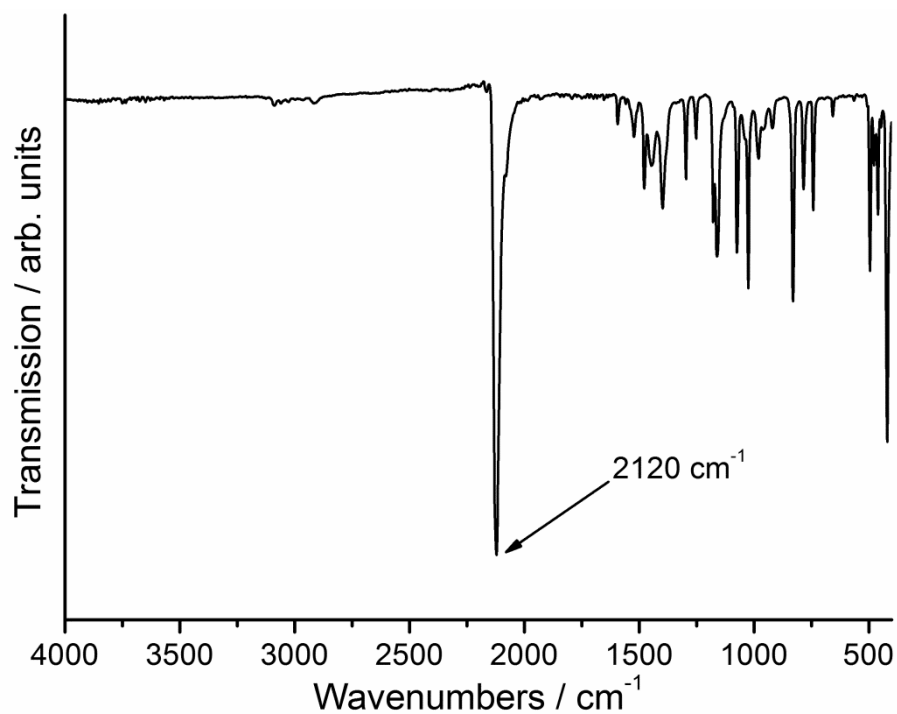


Figure S26. IR spectrum of the residue obtained after the first TG step of the thermal decomposition reaction of **3**.

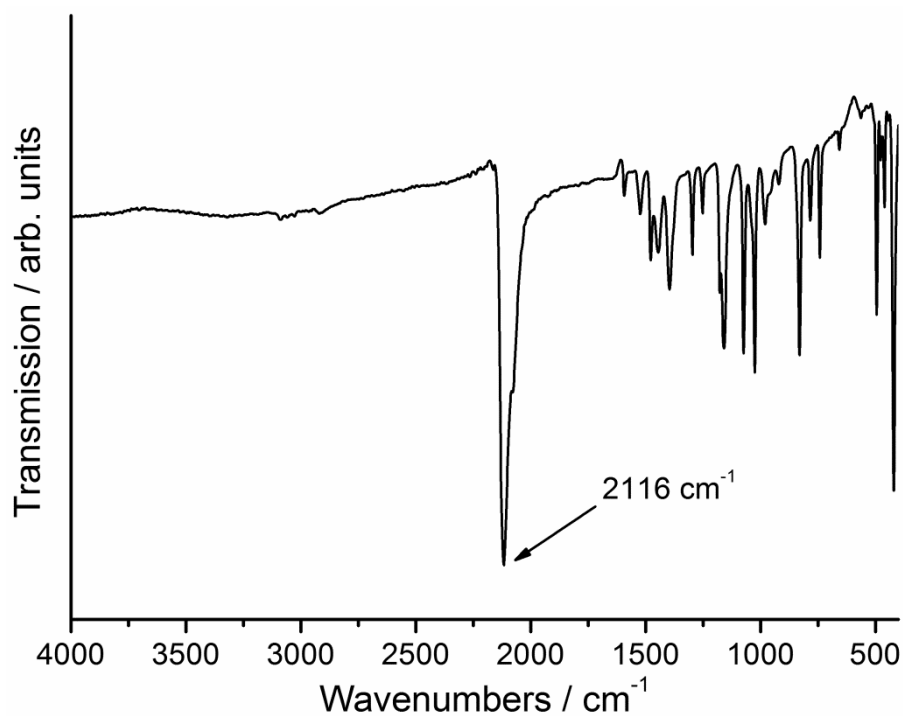


Figure S27. IR spectrum of the residue obtained after the first TG step of the thermal decomposition reaction of **4**.

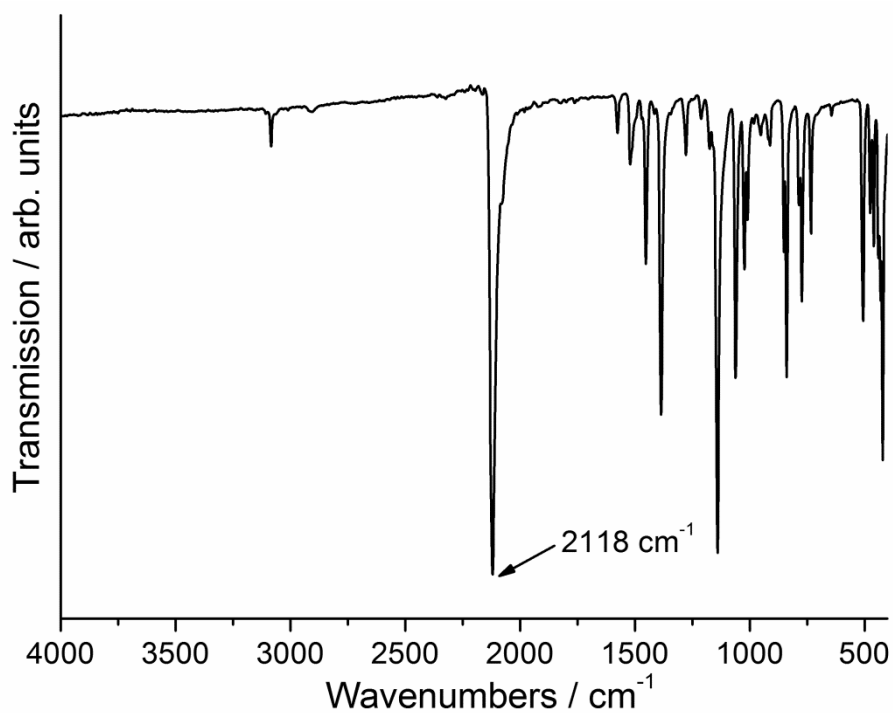


Figure S28. IR spectrum of the residue obtained after the first TG step of the thermal decomposition reaction of **5**.

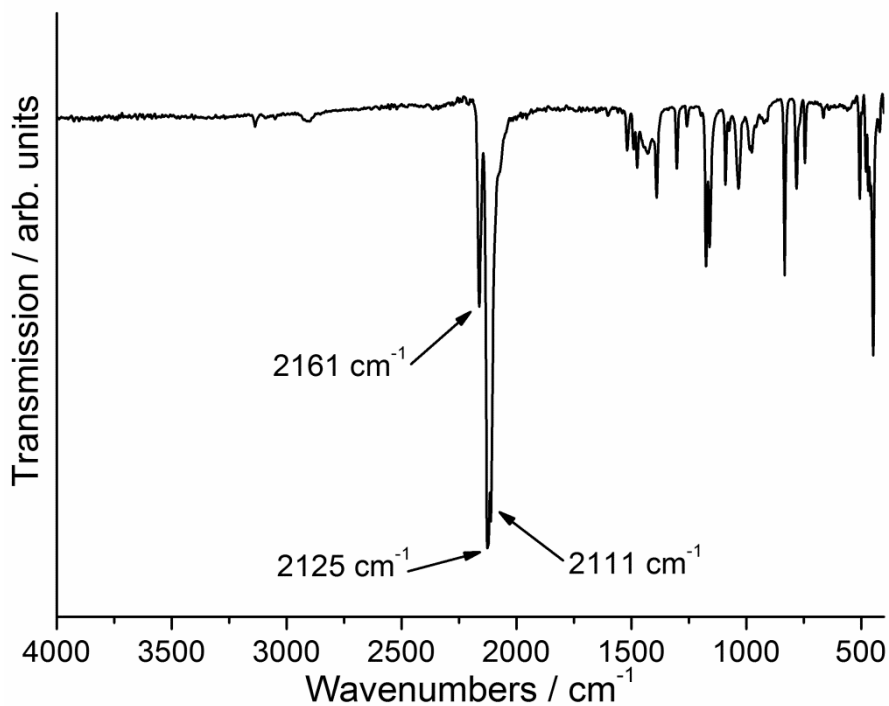


Figure S29. IR spectrum of the residue obtained after the second TG step of the thermal decomposition reaction of **2**.

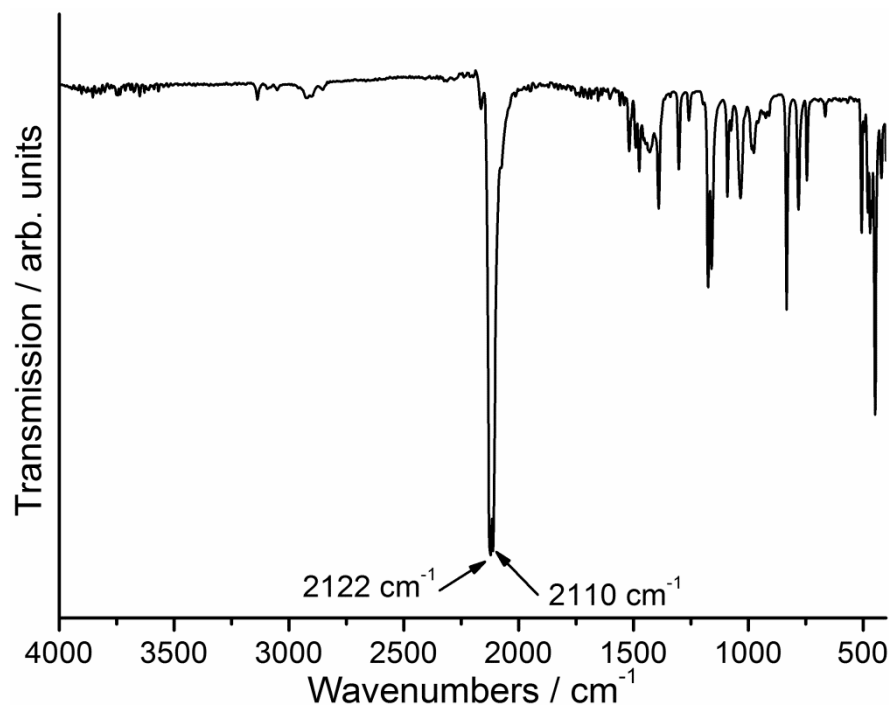


Figure S30. IR spectrum of the residue obtained after the second TG step of the thermal decomposition reaction of **3**.

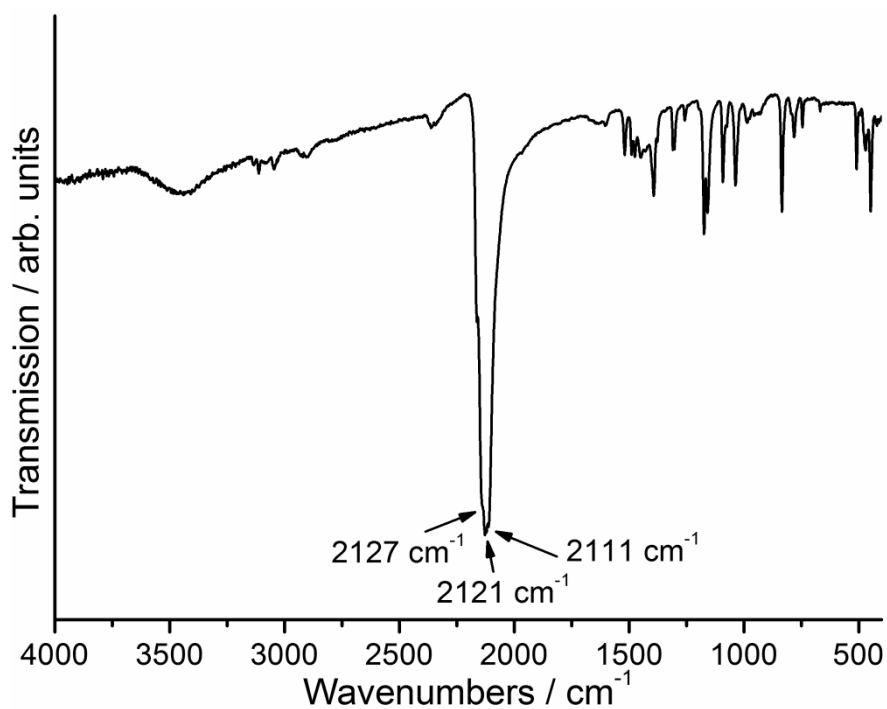


Figure S31. IR spectrum of the residue obtained after the second TG step of the thermal decomposition reaction of **4**.

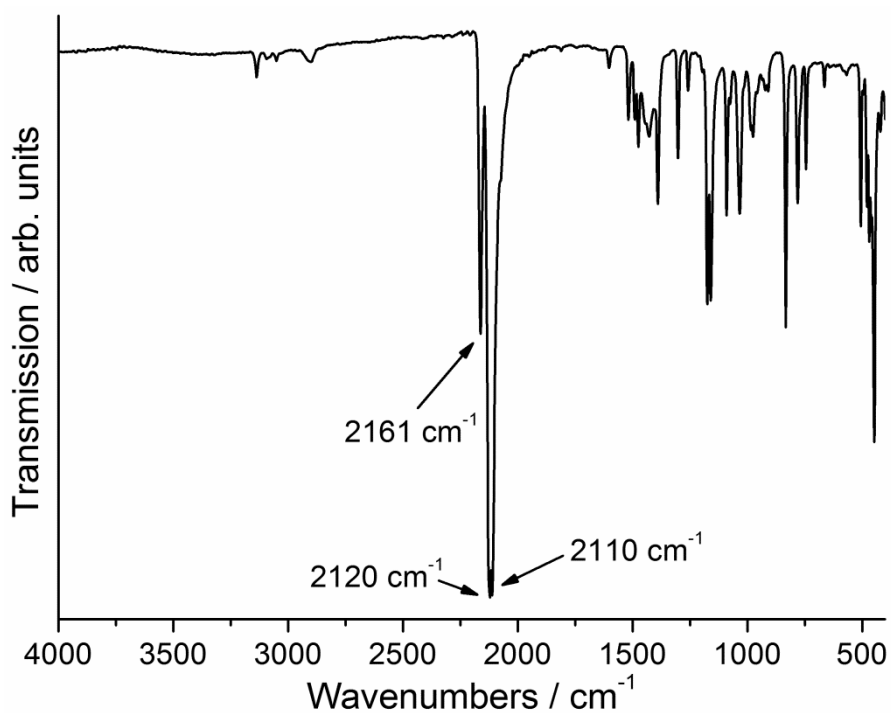


Figure S32. IR spectrum of the residue obtained after the second TG step of the thermal decomposition reaction of **5**.