

A Tail Does Not Always Make a Difference: Assembly of *cds* Nets from Co(NCS)₂ and 1,4-bis(*n*- Alkyloxy)-2,5-bis(3,2':6',3''-terpyridin-4'-yl)benzene Ligands

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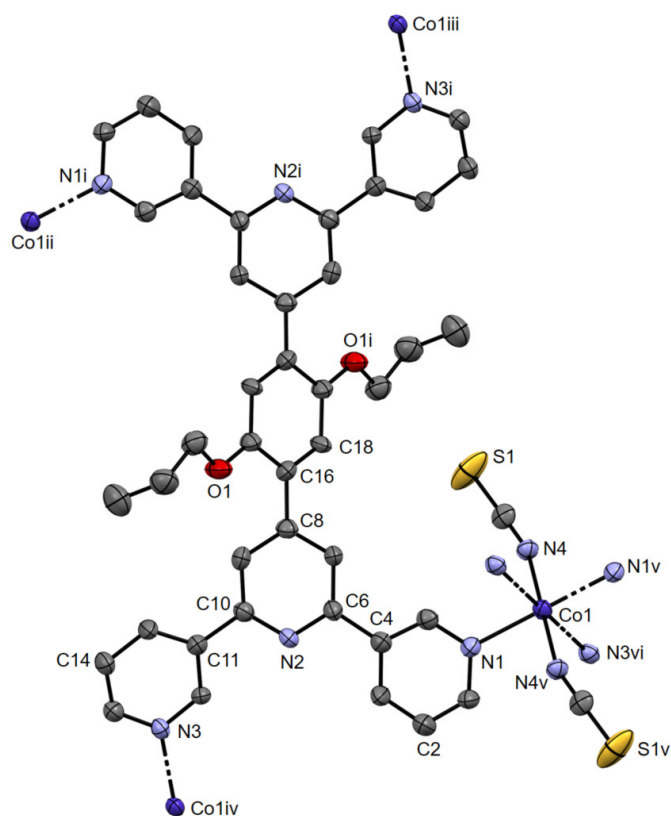


Figure S1. The structure of the asymmetric unit in [Co(NCS)₂(3)]_n·3.5n C₆H₄Cl₂, with symmetry generated atoms. Hydrogen atoms are omitted for clarity; ellipsoids are plotted at 50% probability level. Symmetry codes: i = -1-x, -1-y, -1-z; ii = 1+x, y, 1+z; iii = -1-x, 1/2+y, -3/2-z; iv = -2-x, -1/2+y, -3/2-z; v = -2-x, -1-y, -2-z; vi = -2-x, 1/2+y, -3/2-z.

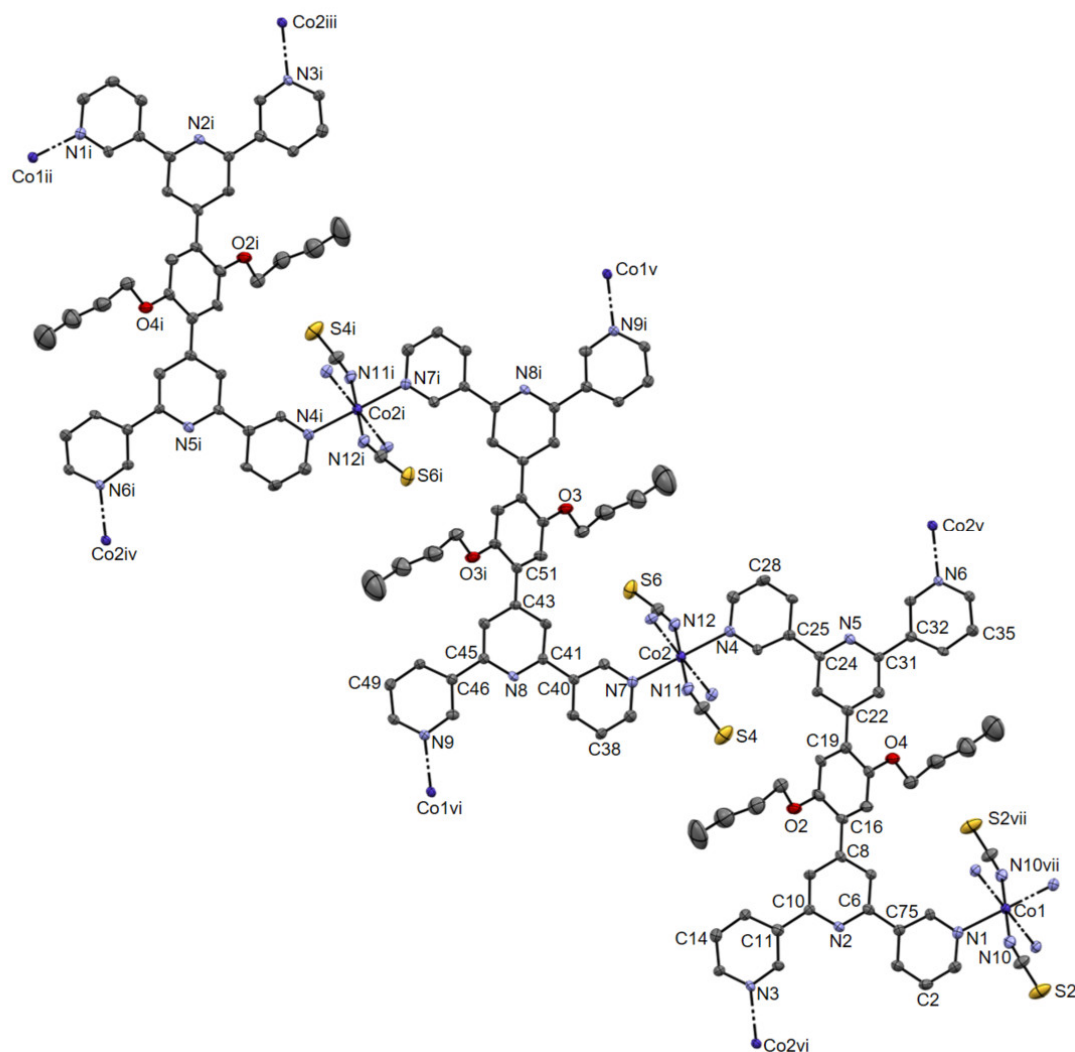


Figure S2. The structure of the asymmetric unit in $[\text{Co}(\text{NCS})_2(\mathbf{4})]_n \cdot 5.5n\text{C}_6\text{H}_4\text{Cl}_2$, with symmetry generated atoms. Hydrogen atoms and solvent molecules are omitted for clarity; ellipsoids are plotted at 50% probability level. Symmetry codes: i = $1-x, 1-y, 2-z$; ii = $-1+x, y, 1+z$; iii = $-1+x, 1/2-y, 1/2+z$; iv = $x, 1/2-y, 1/2+z$; v = $1-x, -1/2+y, 3/2-z$; vi = $2-x, 1/2+y, 3/2-z$; vii = $2-x, 1-y, 1-z$. The sulfur atoms S2, S4 and S6 of the $[\text{NCS}]^-$ units are disordered and have been modelled over sites of 50:30:20%, 60:20:20% and 70:30% occupancies, respectively, and only the major occupancy site is shown. The terminal unit in the $-\text{OButyl}$ chain on O3 is disordered and has been modelled over sites of 75% and 25% occupancies and only the major occupancy site is shown.

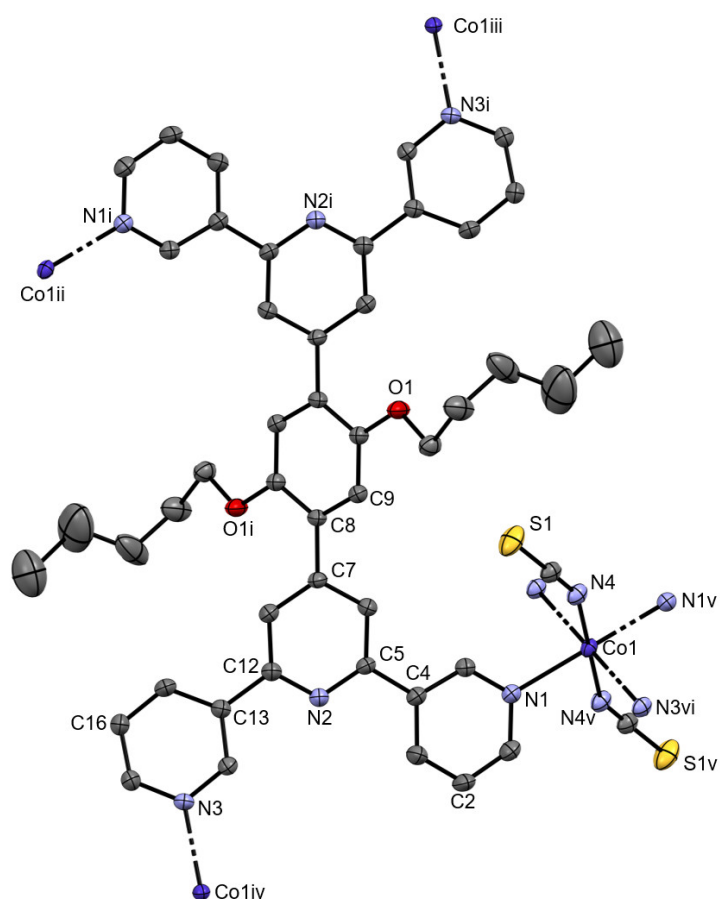


Figure S3. The structure of the asymmetric unit in $[\text{Co}(\text{NCS})_2(\mathbf{5})]_n \cdot 4n\text{C}_6\text{H}_4\text{Cl}_2$, with symmetry generated atoms. Hydrogen atoms and solvent molecules are omitted for clarity; ellipsoids are plotted at 50% probability level. Symmetry codes: i = $1-x, 1-y, 1-z$; ii = $x, y, 1+z$; iii = $1/2-x, 1/2+y, 1/2-z$; iv = $3/2-x, -1/2+y, 1/2-z$; v = $1-x, 1-y, -z$; vi = $3/2-x, 1/2+y, 1/2-z$.

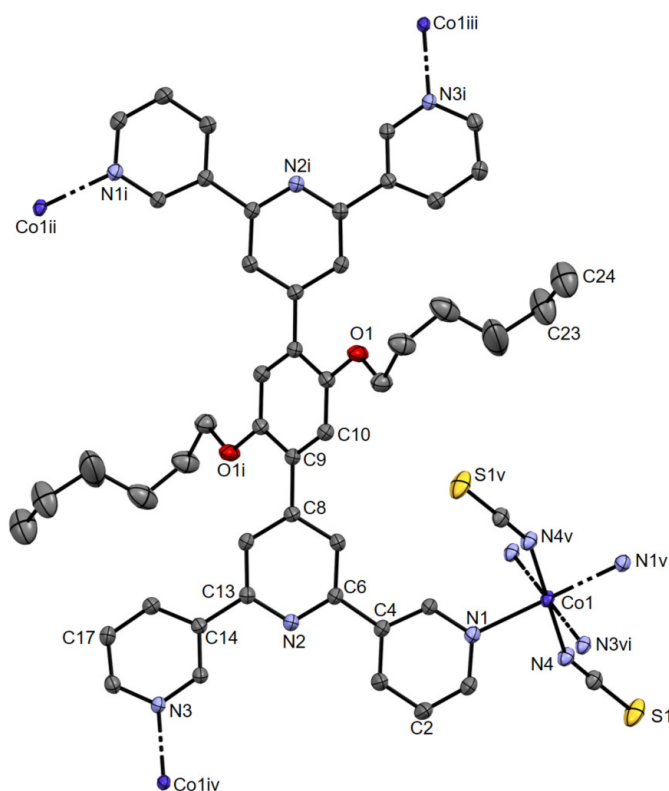


Figure S4. The structure of the asymmetric unit in $[\text{Co}(\text{NCS})_2(\mathbf{6})] \cdot 3.8n\text{C}_6\text{H}_4\text{Cl}_2$, with symmetry generated atoms. Hydrogen atoms and solvent molecules are omitted for clarity; ellipsoids are plotted at 50% probability level. Symmetry codes: i = $1-x, 1-y, 2-z$; ii = $x, y, 1+z$; iii = $1/2-x, 1/2+y, 3/2-z$; iv = $3/2-x, -1/2+y, 3/2-z$; v = $1-x, 1-y, 1-z$; vi = $3/2-x, 1/2+y, 3/2-z$. The terminal units with C23 and C24 in the –OHexyl chain are disordered and have been modelled over sites of 60% and 40% occupancies and only the major one is shown.

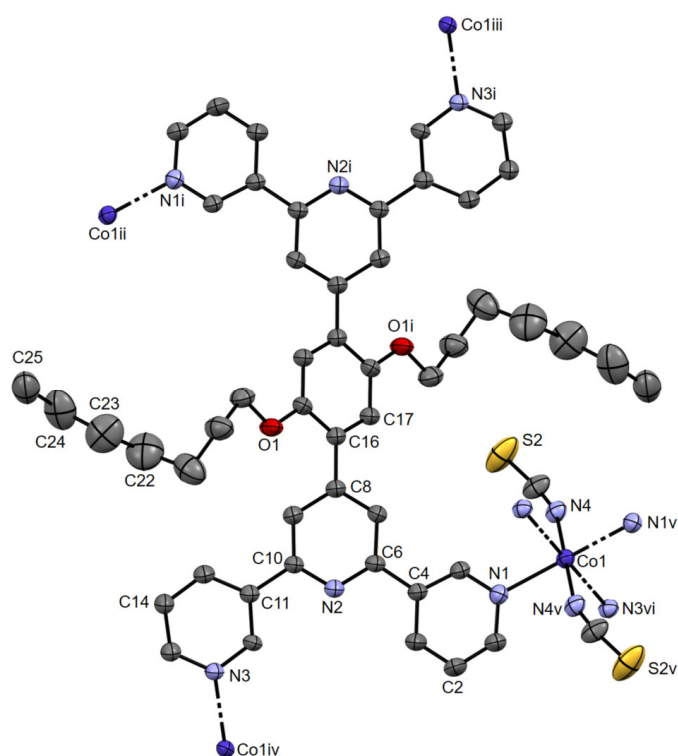


Figure S5. The structure of the asymmetric unit in $[\text{Co}(\text{NCS})_2(\mathbf{7})]_n \cdot 3.1n\text{C}_6\text{H}_4\text{Cl}_2$, with symmetry generated atoms. Hydrogen atoms and solvent molecules are omitted for clarity; ellipsoids are plotted at 50% probability level. Symmetry codes: i = $1-x, 1-y, 1-z$; ii = $x, y, -1+z$; iii = $3/2-x, -1/2+y, 3/2-z$; iv = $1/2-x, 1/2+y, 3/2-z$; v = $1-x, 1-y, 2-z$; vi = $1/2-x, -1/2+y, 3/2-z$. The terminal units with C22, C23, C24 and C25 in the –OHeptyl chain are disordered and have been modelled over sites of 50% and 50% occupancies and only one of the equal occupancy sites is shown. The sulfur S2 of the $[\text{NCS}]^-$ unit is disordered and has been modelled over sites of 80% and 20% occupancies and only the major occupancy site is shown.

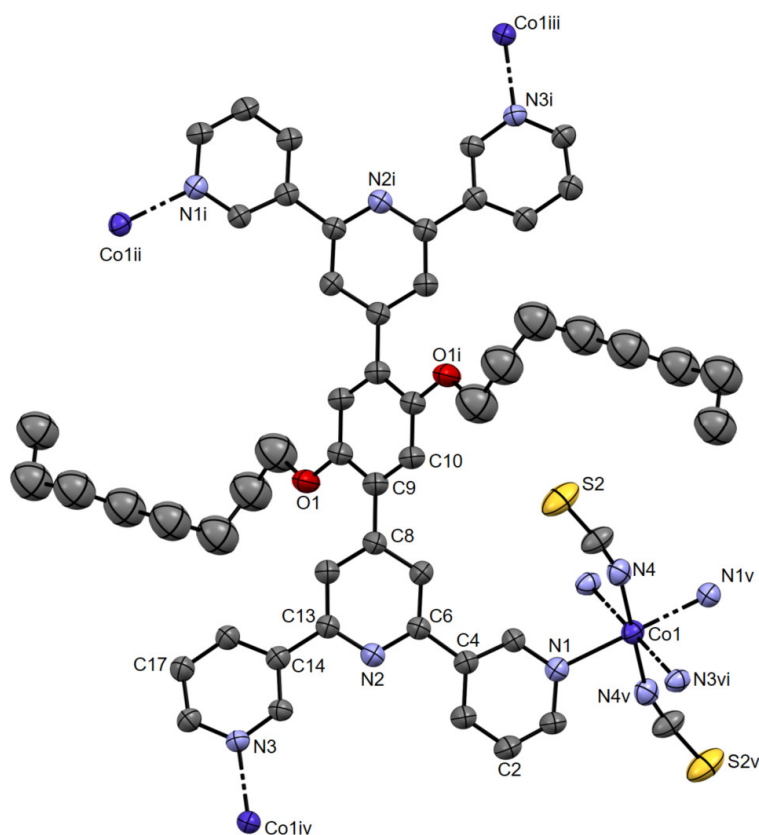


Figure S6. The structure of the asymmetric unit in $[\text{Co}(\text{NCS})_2(\mathbf{8})]_n \cdot 1.6n\text{C}_6\text{H}_4\text{Cl}_2 \cdot 2n\text{MeOH}$, with symmetry generated atoms. Hydrogen atoms and solvent molecules are omitted for clarity; ellipsoids are plotted at 50% probability level. Symmetry codes: i = $-x, 1-y, 1-z$; ii = $x, y, 1+z$; iii = $-1/2-x, 1/2+y, 1/2-z$; iv = $1/2-x, -1/2+y, 1/2-z$; v = $-x, 1-y, -z$; vi = $1/2-x, 1/2+y, 1/2-z$. The sulfur atom S2 of the $[\text{NCS}]^-$ unit is disordered and has been modelled over sites of 80% and 20% occupancies and only the major occupancy site is shown.

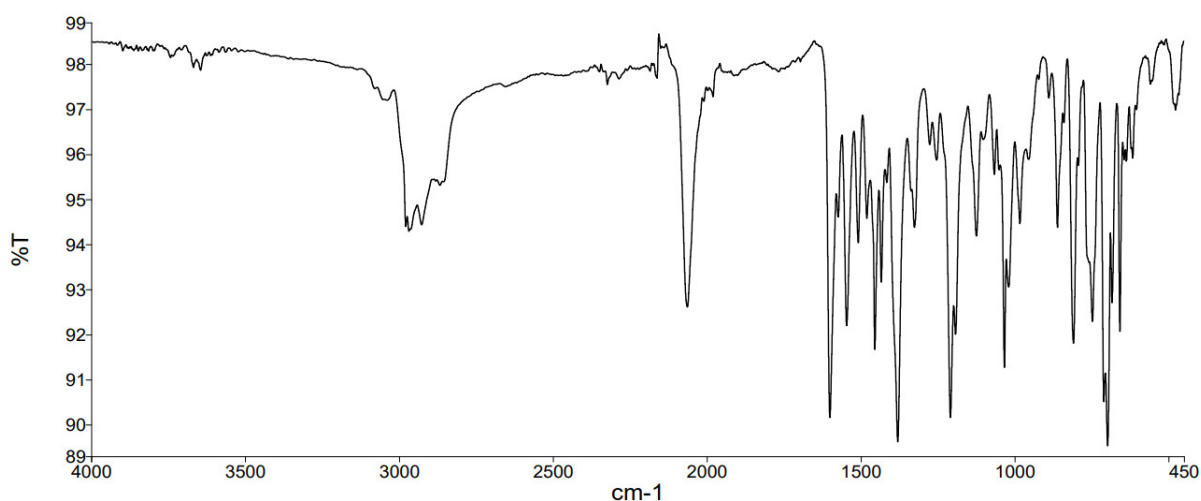


Figure S7. The solid-state FT-IR spectrum of $[\text{Co}(\text{NCS})_2(\mathbf{3})]_n \cdot 3.5n\text{C}_6\text{H}_4\text{Cl}_2$.

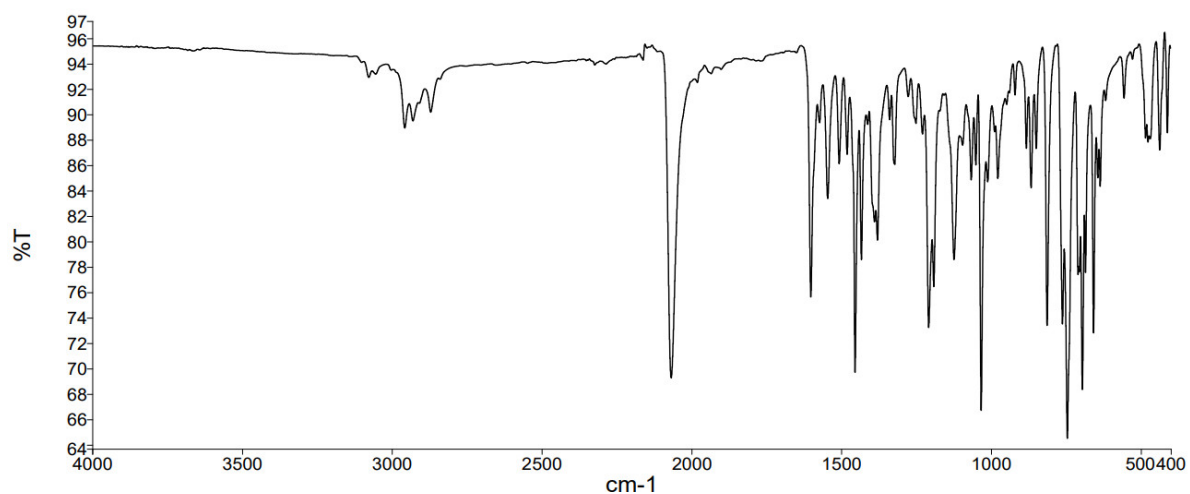


Figure S8. The solid-state FT-IR spectrum of $[\text{Co}(\text{NCS})_2(\mathbf{4})]_n \cdot 5.5n\text{C}_6\text{H}_4\text{Cl}_2$.

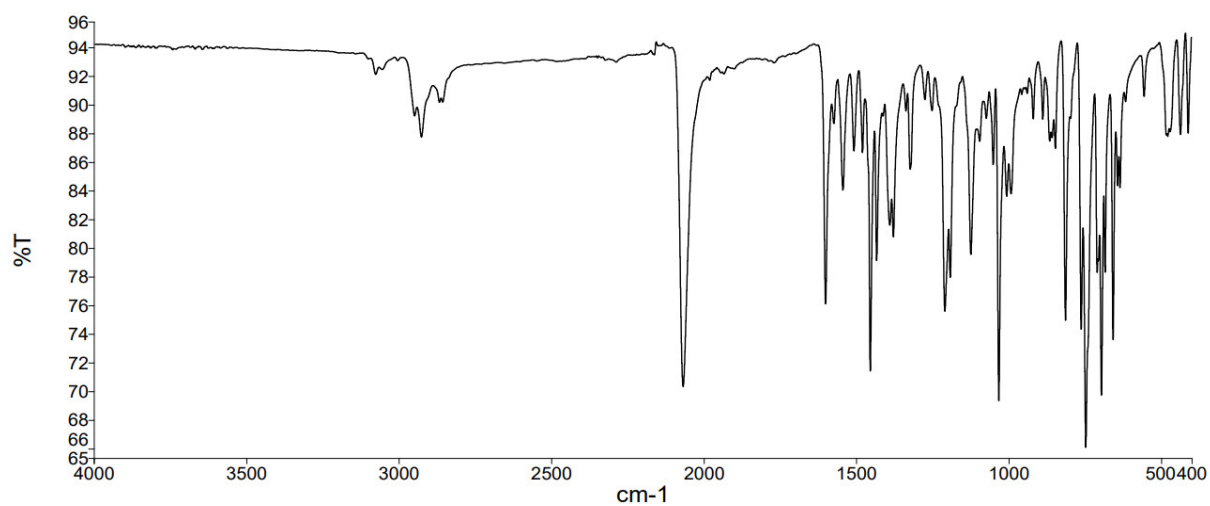


Figure S9. The solid-state FT-IR spectrum of $[\text{Co}(\text{NCS})_2(\mathbf{5})]_n \cdot 4nC_6\text{H}_4\text{Cl}_2$.

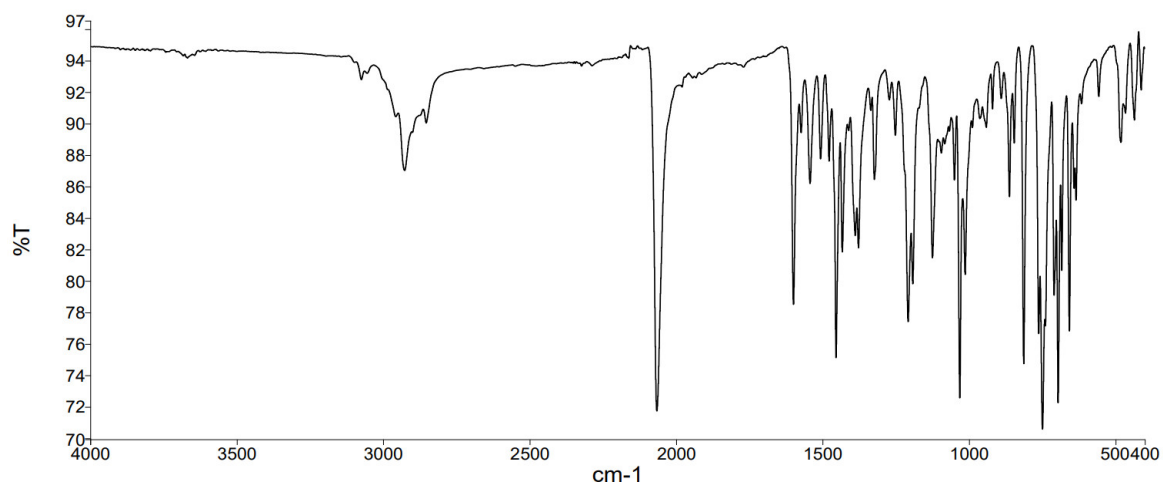


Figure S10. The solid-state FT-IR spectrum of $[\text{Co}(\text{NCS})_2(\mathbf{6})]_n \cdot 3.8nC_6\text{H}_4\text{Cl}_2$.

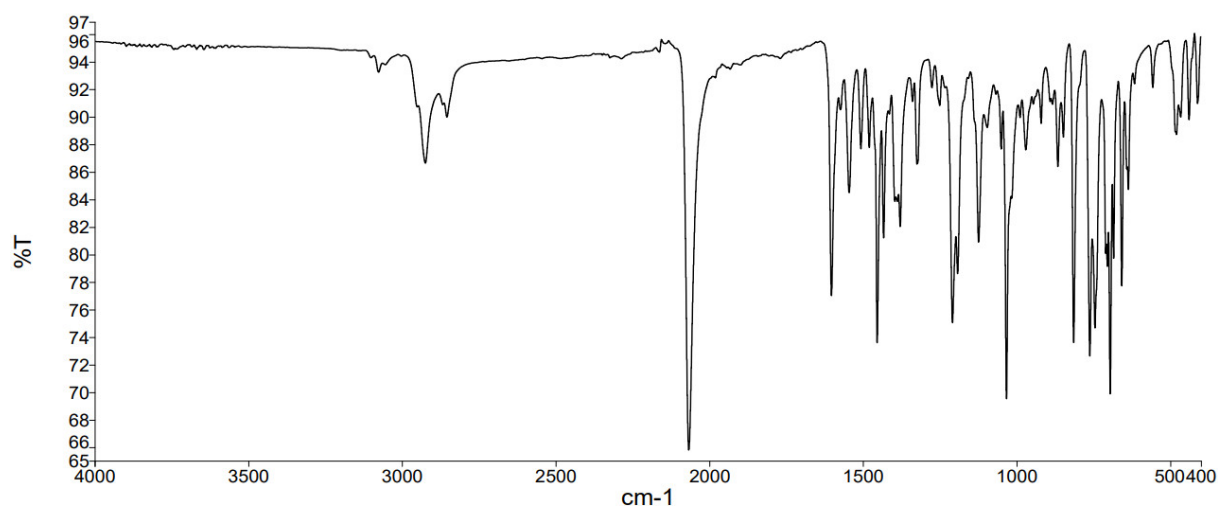


Figure S11. The solid-state FT-IR spectrum of $[\text{Co}(\text{NCS})_2(\mathbf{7})]_n \cdot 3.1n\text{C}_6\text{H}_4\text{Cl}_2$.

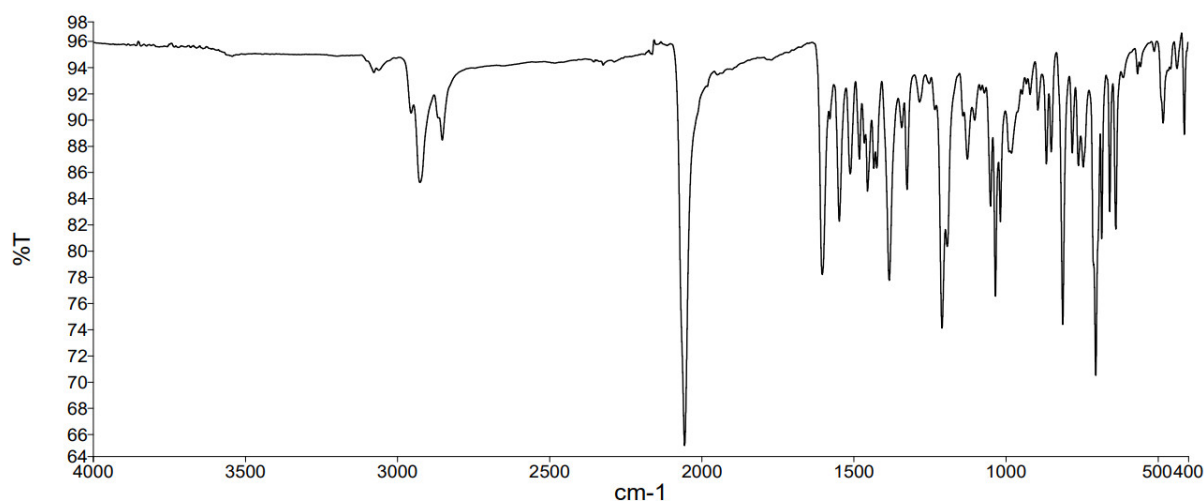


Figure S12. The solid-state FT-IR spectrum of $[\text{Co}(\text{NCS})_2(\mathbf{8})]_n \cdot 1.6n\text{C}_6\text{H}_4\text{Cl}_2 \cdot 2n\text{MeOH}$.

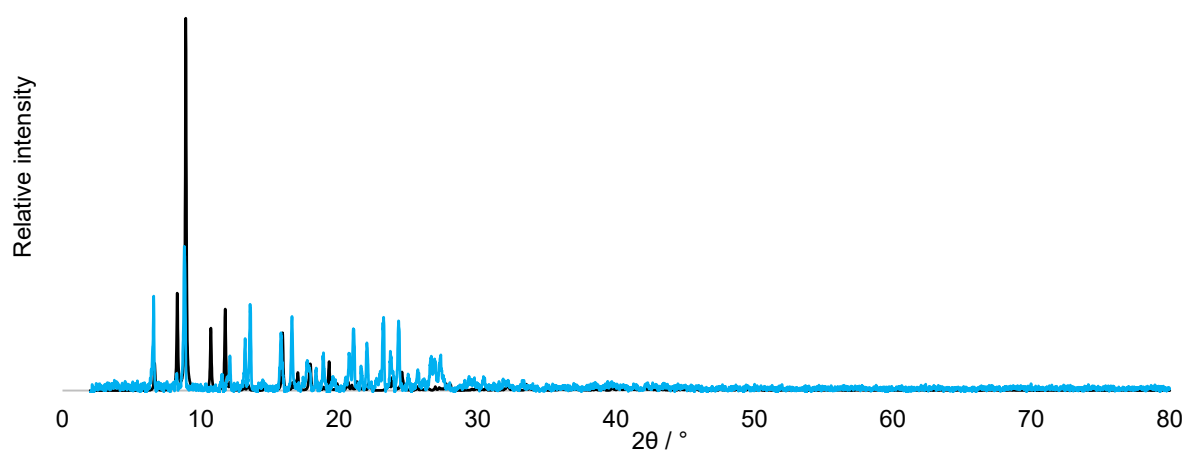


Figure S13. Overlay of the experimental (blue) PXRD (298 K) for the bulk material and that predicted (black) from the single crystal structure (150 K) of $[\text{Co}(\text{NCS})_2(\mathbf{3})]_n \cdot 3.5n\text{C}_6\text{H}_4\text{Cl}_2$.

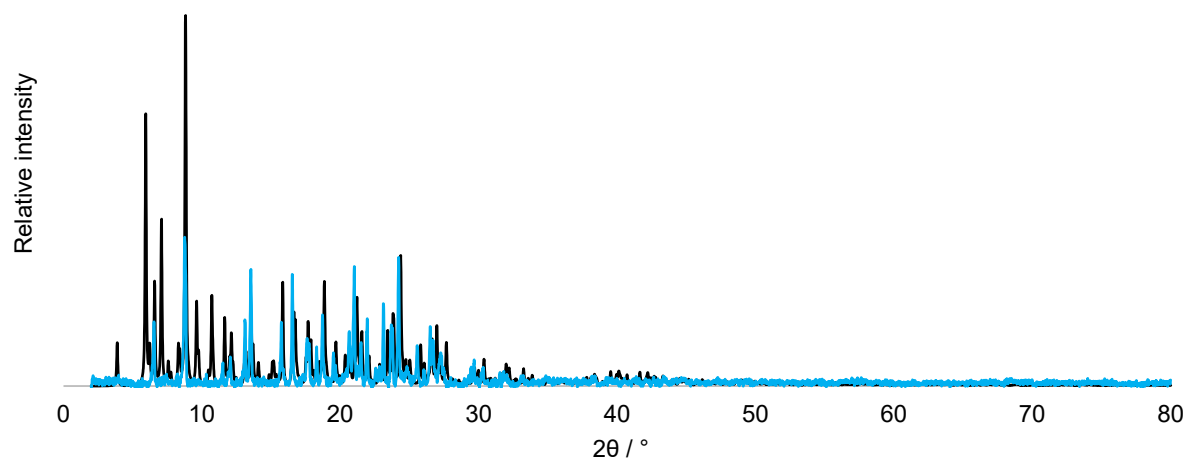


Figure S14. Overlay of the experimental (blue) PXRD (298 K) for the bulk material and that predicted (black) from the single crystal structure (150 K) of $[\text{Co}(\text{NCS})_2(4)]_n \cdot 5.5n\text{C}_6\text{H}_4\text{Cl}_2$.

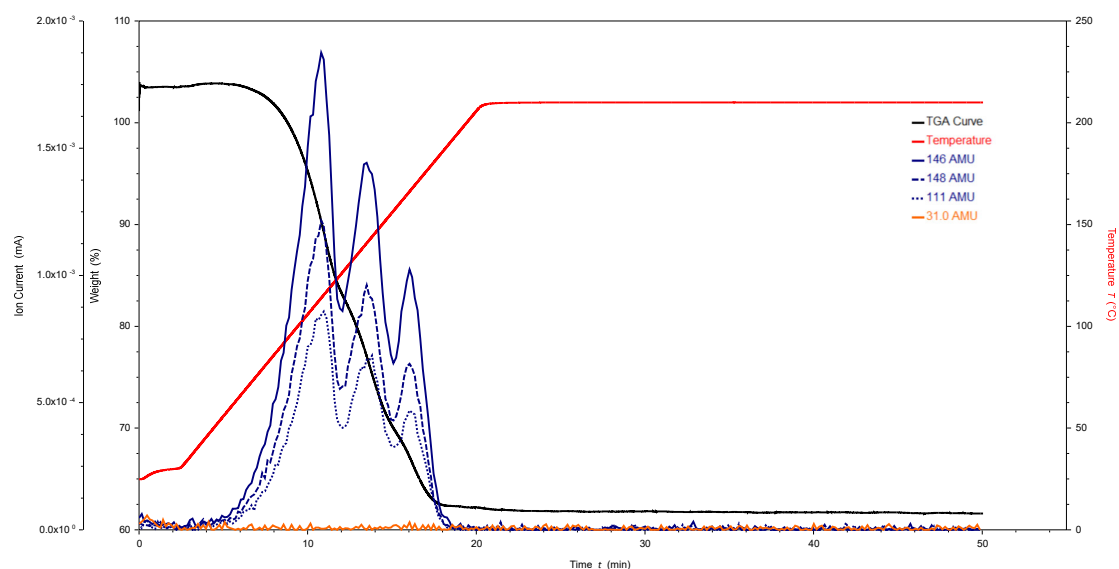


Figure S15. TGA and mass spectrometric traces for the analysis of $[\text{Co}(\text{NCS})_2(3)]_n \cdot 3.5n\text{C}_6\text{H}_4\text{Cl}_2$. Red: temperature vs. time; black: weight of sample vs. time; dark blue: mass detection for m/z 146, 148 and 111; orange: mass detection for m/z 31.0.

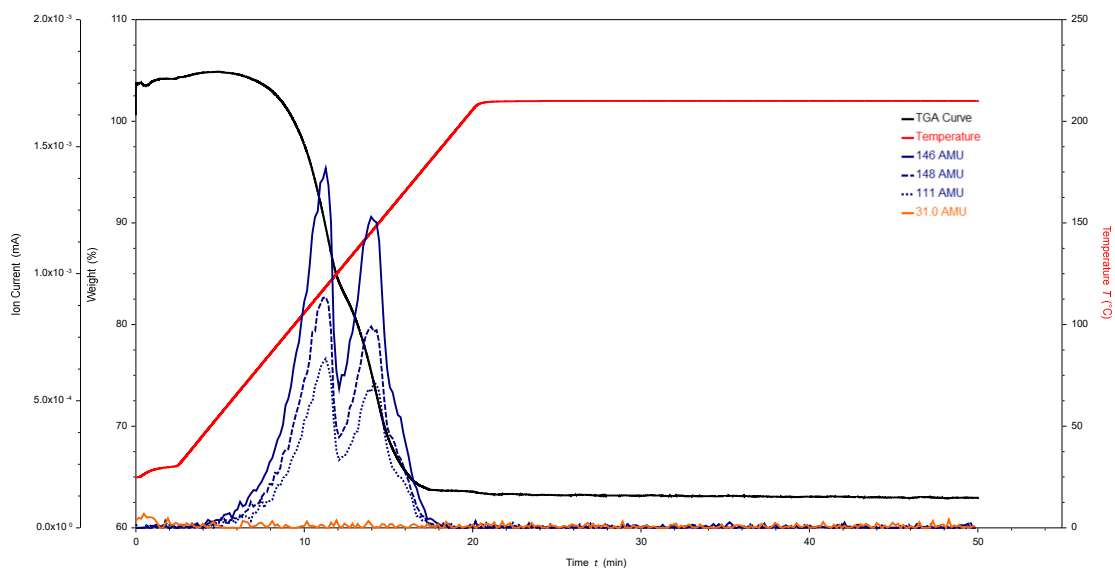


Figure S16. TGA and mass spectrometric traces for the analysis of $[\text{Co}(\text{NCS})_2(\mathbf{4})]_n \cdot 5.5n\text{C}_6\text{H}_4\text{Cl}_2$. Red: temperature vs. time; black: weight of sample vs. time; dark blue: mass detection for m/z 146, 148 and 111; orange: mass detection for m/z 31.0.

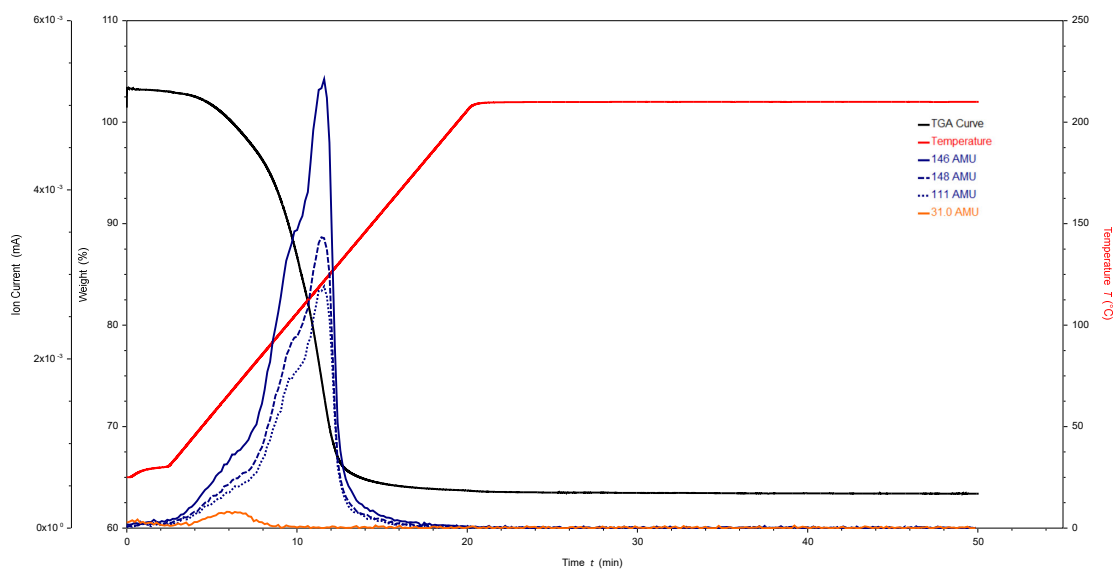


Figure S17. TGA and mass spectrometric traces for the analysis of $[\text{Co}(\text{NCS})_2(\mathbf{6})]_n \cdot 3.8n\text{C}_6\text{H}_4\text{Cl}_2$. Red: temperature vs. time; black: weight of sample vs. time; dark blue: mass detection for m/z 146, 148 and 111; orange: mass detection for m/z 31.0.