Electronic Supplementary Information for Dalton Transactions

Supporting Information

In situ Solid State Formation of Copper(I) Coordination Polymers by Thermal Reduction of Copper(II) Precursor Compounds: Structure and Reactivity of $[Cu(NCS)_2(pyrimidine)_2]_n$

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- Selected bond lengths and angles for **1**.

  (Table S1)

- Experimental and calculated XRPD patterns of compounds **1**, **2** and **3**.

  (Figure S1 to S3)

- IR spectroscopic data of compounds **1**, **2**, **3** and all intermediates obtained in the first hearting step.

  (Figure S4 to S9)

- TG curve of compound **2**.

  (Figure S10)

- Experimental XRPD pattern of the intermediate obtained in the first heating step of compound **2** in comparison with the experimental XRPD pattern of copper(I) thiocyanate and calculated XRPD pattern of $[(CuNCS)_2(pyrazine)]_n$.

  (Figure S11)

Table S1. Selected bond lengths [Å] and angles [deg] for **1**.

Cu(1)-N(1)	2.040(2)	Cu(2)-N(41)	1.949(3)
Cu(1)-N(11)	2.054(2)	Cu(2)-N(21)	2.060(3)
Cu(1)-N(51)	1.957(3)	Cu(2)-S(51)	2.9598(9)
Cu(1)-N(61)	1.954(3)	Cu(3)-N(31)	2.061(3)
Cu(1)-S(41)	2.8081(10)	Cu(3)-N(71)	1.930(3)
Cu(1)-S(71)	3.1146(10)	Cu(3)-S(61)	2.9861(9)
N(61)-Cu(1)-N(51)	177.48(14)	N(41)-Cu(2)-N(41A)	180
N(61)-Cu(1)-N(1)	88.98(13)	N(41)-Cu(2)-N(21A)	89.71(12)
N(51)-Cu(1)-N(1)	90.16(13)	N(41)-Cu(2)-N(21)	90.29(12)
N(61)-Cu(1)-N(11)	90.18(13)	N(41A)-Cu(2)-N(21)	89.71(12)
N(51)-Cu(1)-N(11)	90.47(13)	N(21A)-Cu(2)-N(21)	180
N(1)-Cu(1)-N(11)	174.86(12)	N(71B)-Cu(3)-N(71)	180
N(61)-Cu(1)-S(41)	89.73(9)	N(71B)-Cu(3)-N(31B)	90.28(12)
N(51)-Cu(1)-S(41)	92.68(9)	N(71)-Cu(3)-N(31B)	89.72(12)
N(1)-Cu(1)-S(41)	93.19(9)	N(71)-Cu(3)-N(31)	90.28(12)
N(11)-Cu(1)-S(41)	91.87(9)		
N(41)-C(41)	1.159(4)	C(41)-S(41)	1.635(3)
C(41)-N(41)-Cu(2)	168.1(3)	N(41)-C(41)-S(41)	179.8(4)
C(41)-S(41)-Cu(1)	98.2(1)		
N(51)-C(51)	1.161(4)	C(51)-S(51)	1.638(3)
C(51)-N(51)-Cu(1)	165.3(3)	N(51)-C(51)-S(51)	179.5(3)
C(51)-S(51)-Cu(2)	97.6(1)		
N(61)-C(61)	1.163(4)	C(61)-S(61)	1.641(3)
C(61)-N(61)-Cu(1)	173.2(3)	N(61)-C(61)-S(61)	178.8(3)
C(61)-S(61)-Cu(3)	96.9(1)		
N(71)-C(71)	1.170(4)	S(71)-C(71)	1.627(3)
C(71)-N(71)-Cu(3)	169.6(3)	N(71)-C(71)-S(71)	179.1(3)
C(71)-S(71)-Cu(1)	95.2(1)		

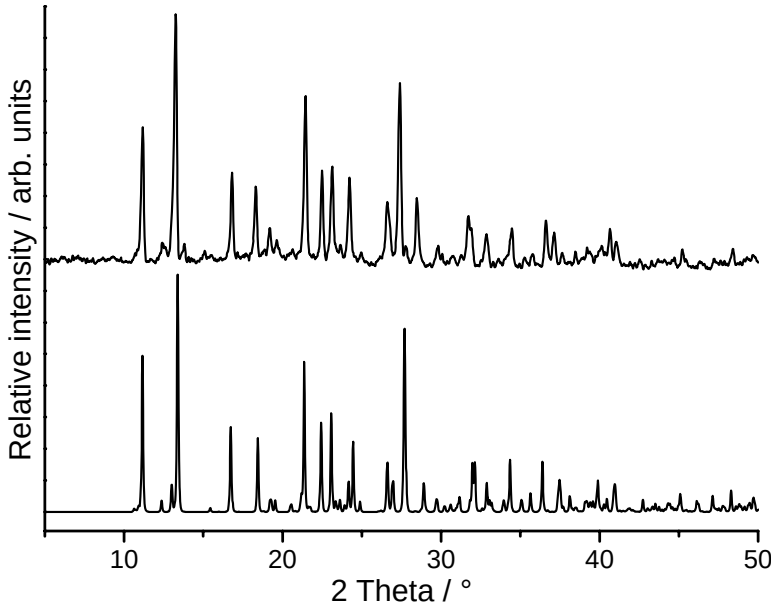

Figure S1. Experimental (top) and calculated (bottom) XRPD pattern of compound **1**.

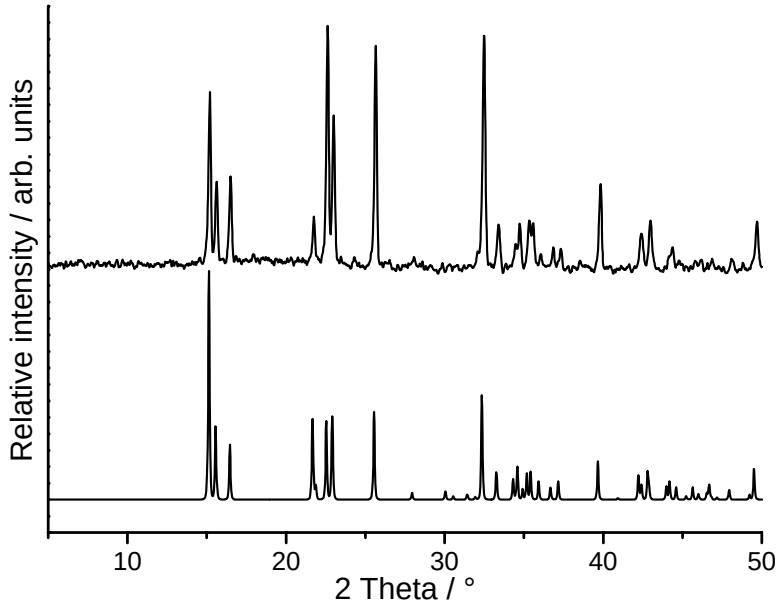

Figure S2. Experimental (top) and calculated (bottom) XRPD pattern of compound **2**.

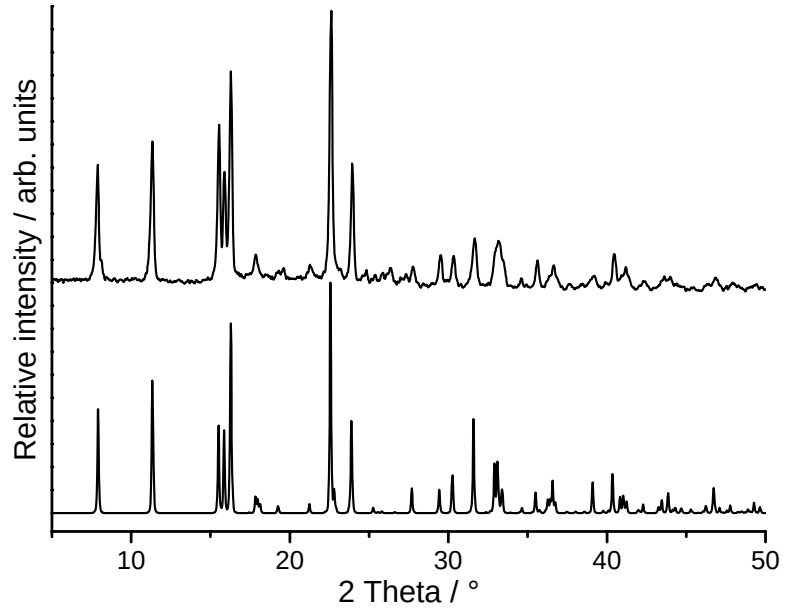

Figure S3. Experimental (top) and calculated (bottom) XRPD pattern of compound **3**.

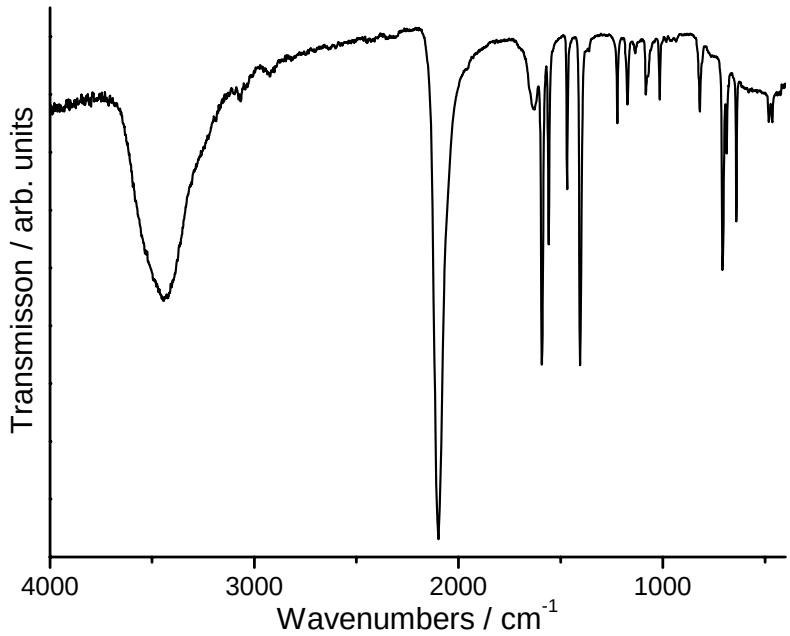

Figure S4. IR spectroscopic data of compound **1**.

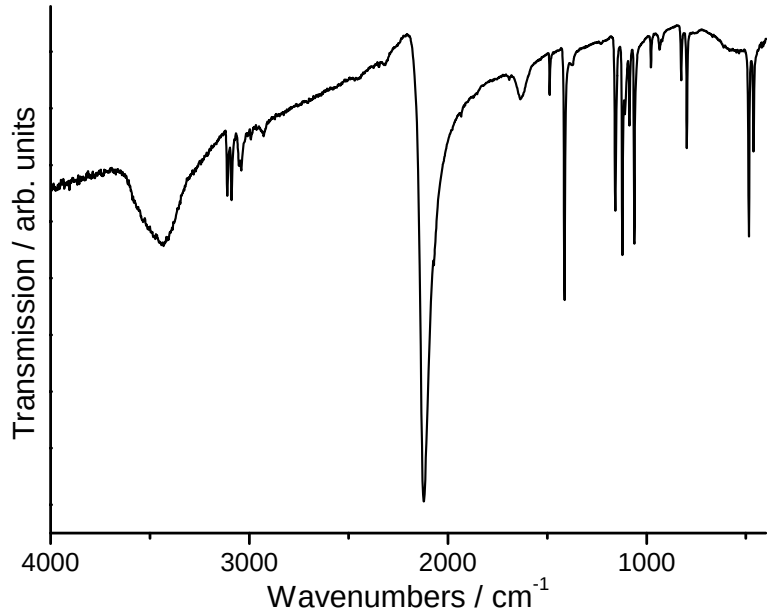

Figure S5. IR spectroscopic data of compound **2**.

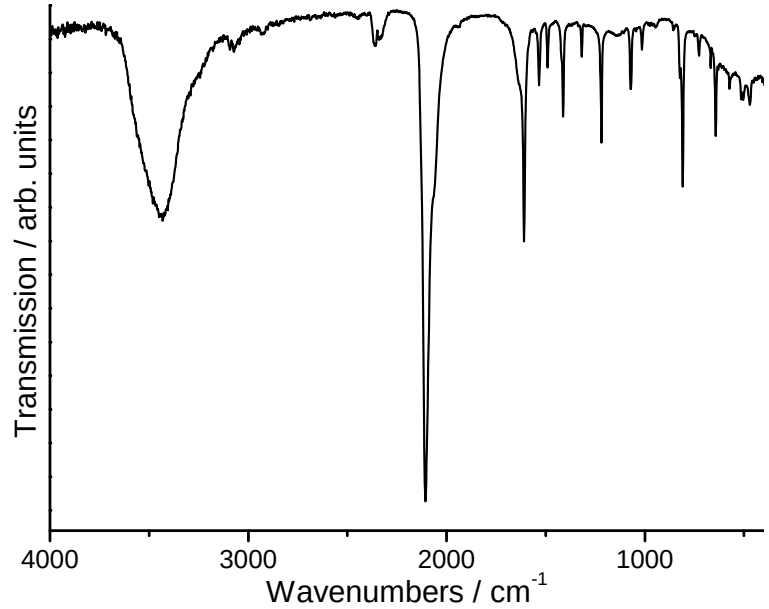

Figure S6. IR spectroscopic data of compound **3**.

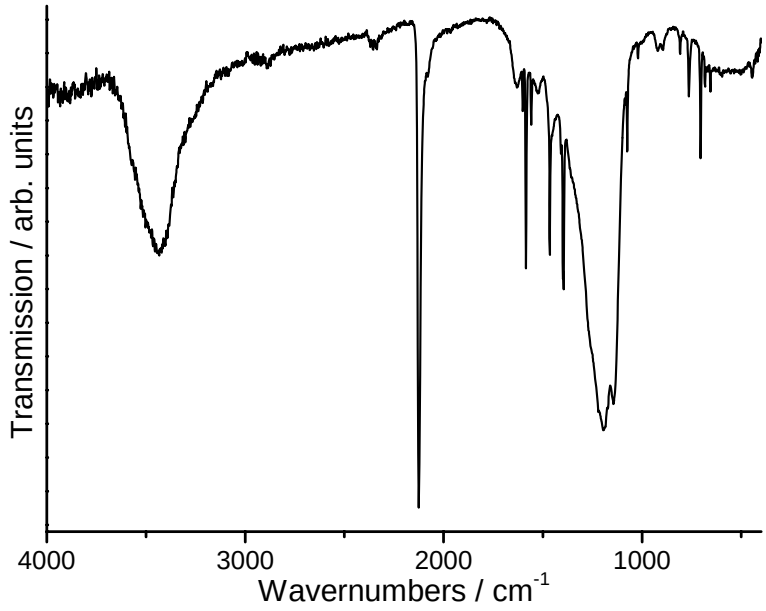

Figure S7. IR spectroscopic data of the intermediate obtained in the first hearting step of compound **1**.

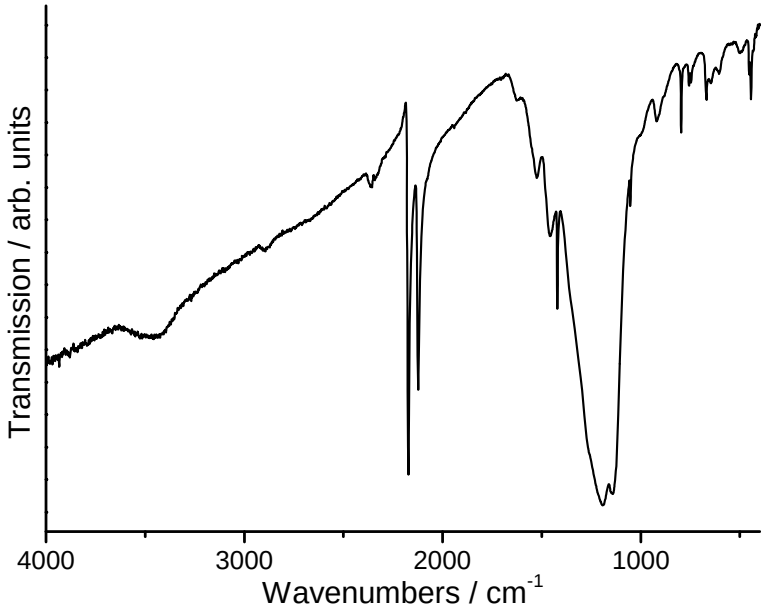

Figure S8. IR spectroscopic data of the intermediate obtained in the first hearting step of compound **2**.

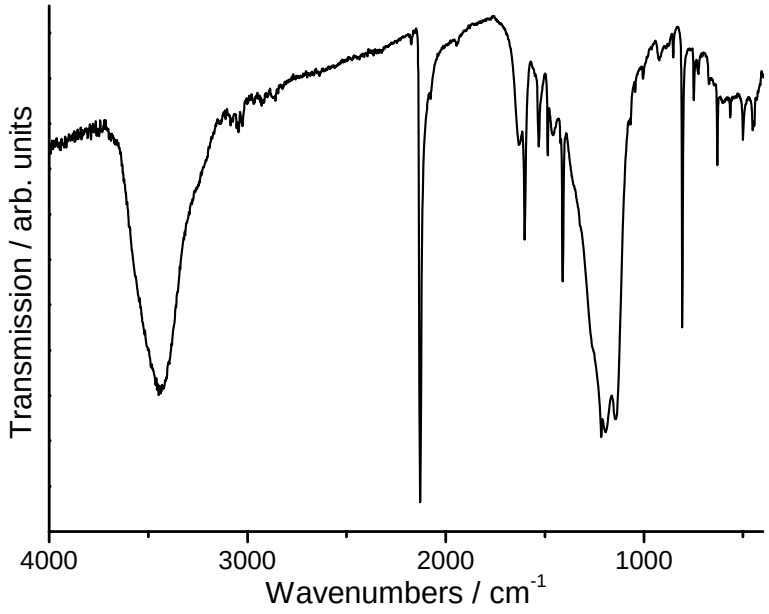

Figure S9. IR spectroscopic data of the intermediate obtained in the first hearting step of compound **3**.

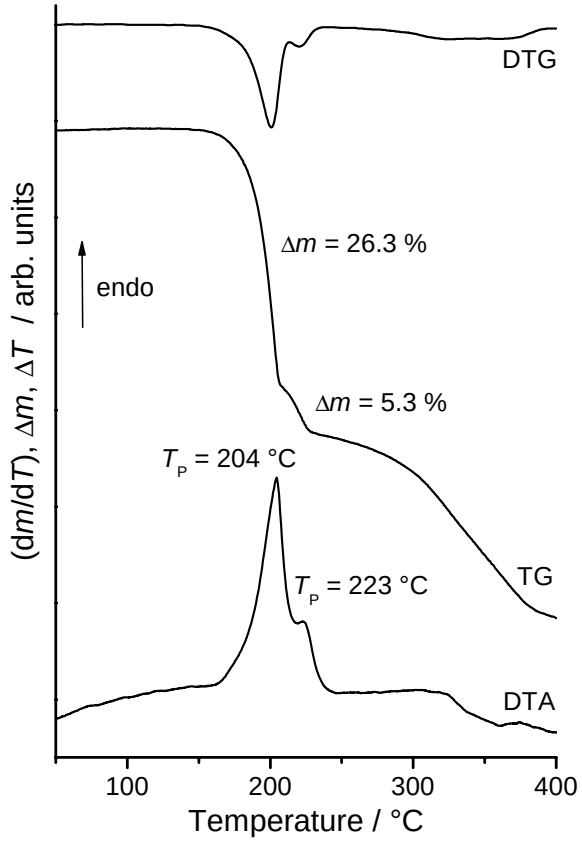

Figure S10. DTG, TG and DTA curves for compound **2**. Heating rate = 4 °C/min; given are the mass changes (%) and the peak temperatures T_P (°C).

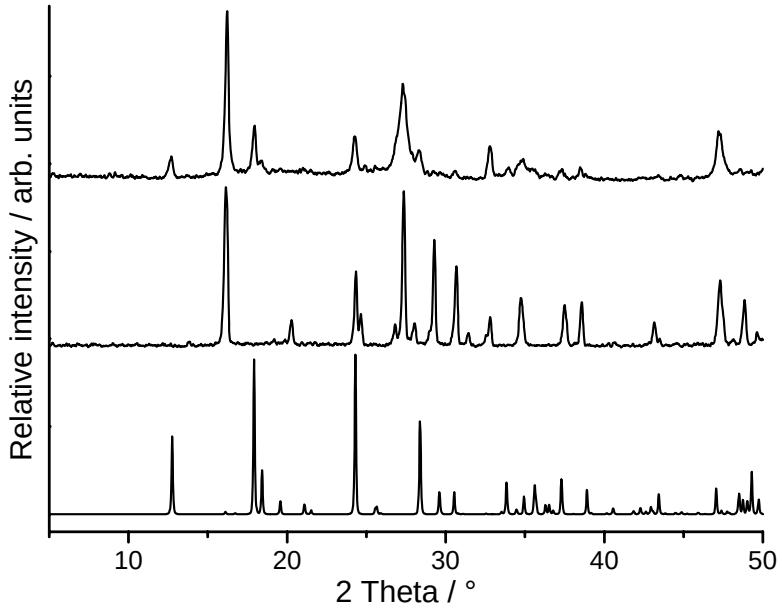

Figure S11. Experimental XRPD pattern of the intermediate obtained in the first heating step of compound **2** (top), experimental XRPD pattern of copper(I) thiocyanate obtained from Alfa Aesar (middle) and calculated XRPD pattern of $[(CuNCS)_2(pyrazine)]_n$ (bottom).