Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

New Cadmium Thio- and Selenocyanato Coordination Compounds: Structural Snapshots on the Reaction Pathway to more Condensed Anionic Networks

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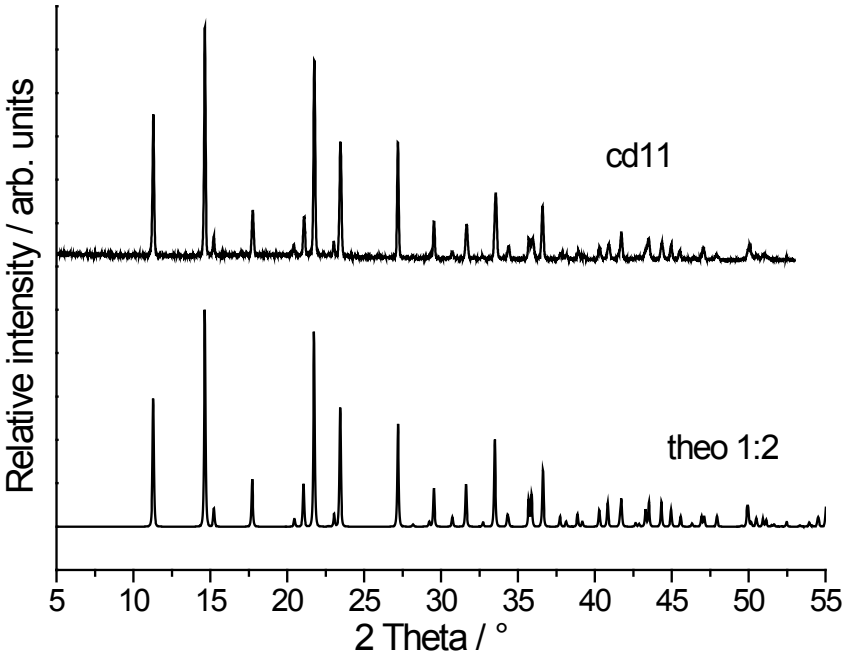

Figure S1. Experimental (top) and calculated (bottom) XRPD pattern for compound **1A**.

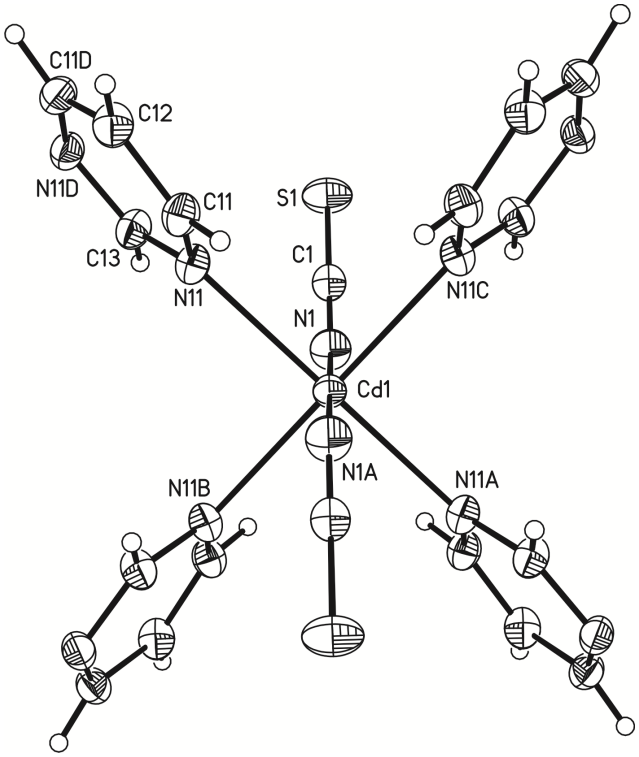

Figure S2. Crystal structure of compound **1A** with labeling and displacement ellipsoids drawn at the 50% probability level.

Table S1. Selected bond lengths [Å] and angles [°] for compound **1A**.

Cd(1)-N(1A)	2.224(5)	Cd(1)-N(11)	2.423(3)
Cd(1)-N(1)	2.224(5)	Cd(1)-N(11B)	2.423(3)
Cd(1)-N(11A)	2.423(3)	Cd(1)-N(11C)	2.423(3)
N(1A)-Cd(1)-N(1)	180.0(3)	N(11A)-Cd(1)-N(11)	180.0(2)
N(1A)-Cd(1)-N(11A)	91.08(14)	N(11A)-Cd(1)-N(11B)	88.07(17)
N(1)-Cd(1)-N(11A)	88.92(14)	N(11)-Cd(1)-N(11B)	91.93(17)
N(1A)-Cd(1)-N(11)	88.92(14)	N(11A)-Cd(1)-N(11C)	91.93(17)
N(1)-Cd(1)-N(11)	91.08(14)	N(11)-Cd(1)-N(11C)	88.07(17)
N(1A)-Cd(1)-N(11B)	91.08(14)	N(11B)-Cd(1)-N(11C)	180.0
N(1)-Cd(1)-N(11B)	88.92(14)	N(1)-Cd(1)-N(11C)	91.08(14)
N(1A)-Cd(1)-N(11C)	88.92(14)		

Symmetry transformations used to generate equivalent atoms:
A = -x, -y+1, -z; B = x, -y+1, -z; C = -x, y, z; D = -x+1/2, y, -z+1/2.

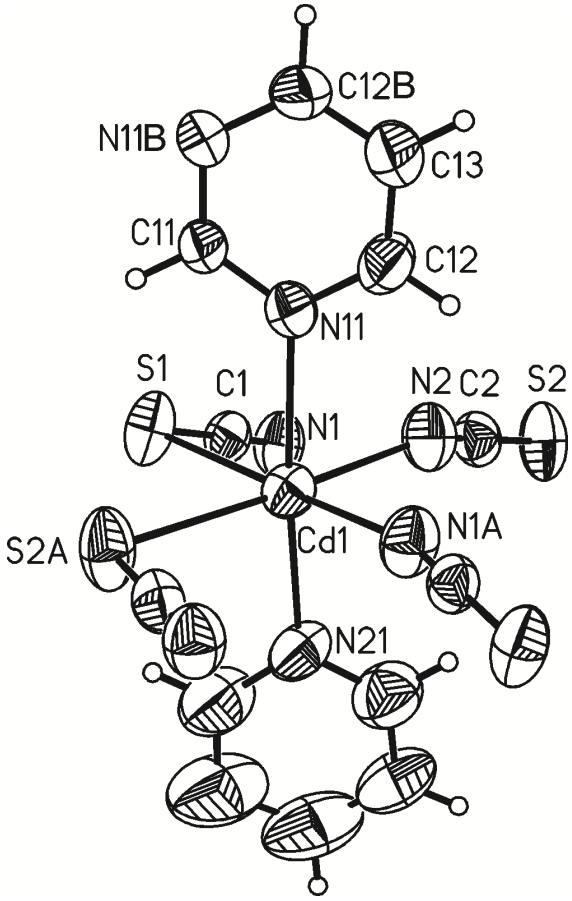

Figure S3. Crystal structure of compound **1B** with labeling and displacement ellipsoids drawn at the 50% probability level.

Table S2. Selected bond lengths [Å] and angles [°] for compound **1B**.

Cd(1)-N(1A)	2.284(6)	Cd(1)-N(11)	2.406(5)
Cd(1)-N(2)	2.319(6)	Cd(1)-S(2A)	2.674(2)
Cd(1)-N(21)	2.358(6)	Cd(1)-S(1)	2.7210(19)
N(1A)-Cd(1)-N(2)	88.11(18)	N(21)-Cd(1)-S(2A)	93.32(18)
N(1A)-Cd(1)-N(21)	93.8(2)	N(11)-Cd(1)-S(2A)	93.45(13)
N(2)-Cd(1)-N(21)	87.7(2)	N(1A)-Cd(1)-S(1)	176.36(18)
N(1A)-Cd(1)-N(11)	87.9(2)	N(2)-Cd(1)-S(1)	94.24(15)
N(2)-Cd(1)-N(11)	85.4(2)	N(21)-Cd(1)-S(1)	89.07(16)
N(21)-Cd(1)-N(11)	172.8(2)	N(11)-Cd(1)-S(1)	89.48(13)
N(1A)-Cd(1)-S(2A)	95.18(14)	S(2A)-Cd(1)-S(1)	82.41(6)
N(2)-Cd(1)-S(2A)	176.49(15)		

Symmetry transformations used to generate equivalent atoms:

A: x-1/2,-y+1/2,-z+1; B: x+1/2,-y+1/2,-z+1; C: -x+1,-y+1,z.

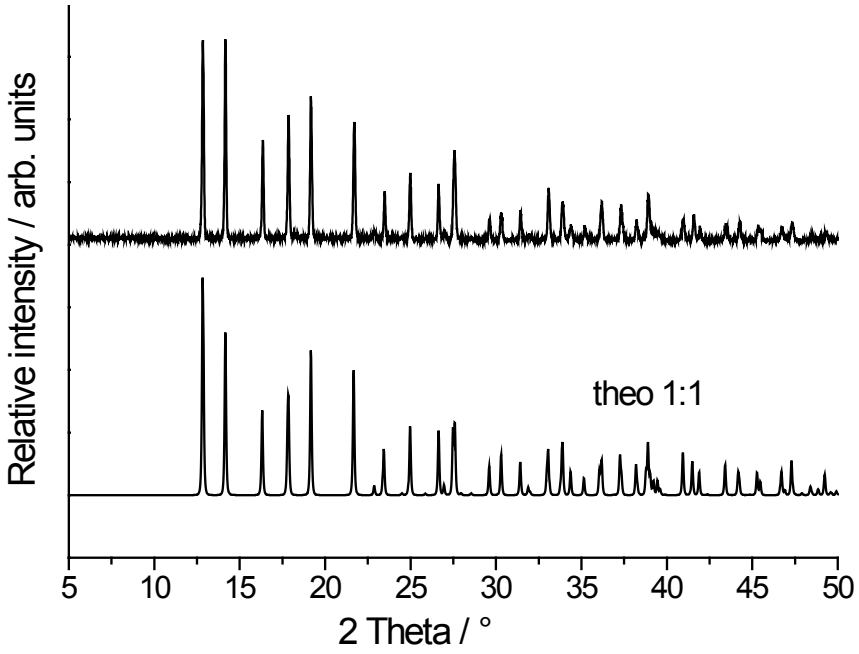

Fig. S4 Experimental and calculated XRPD pattern for compound **1CI**.

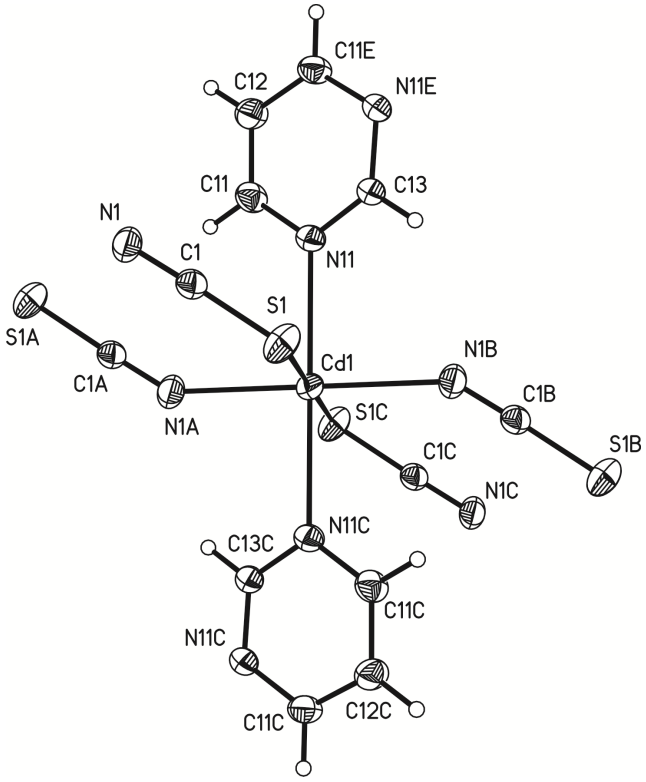

Figure S5. Crystal structure of compound **1CI** with labeling and displacement ellipsoids drawn at the 50% probability level.

Table S3. Selected bond lengths [Å] and angles [°] for compound **1CI**.

Cd(1)-N(1A) 2.2935(17)	Cd(1)-N(11C) 2.4160(15)
Cd(1)-N(1B) 2.2935(17)	Cd(1)-S(1) 2.7030(7)
Cd(1)-N(11) 2.4160(15)	Cd(1)-S(1C) 2.7030(7)
N(1A)-Cd(1)-N(1B) 180.00(8)	N(11)-Cd(1)-S(1) 85.39(4)
N(1A)-Cd(1)-N(11) 90.47(6)	N(11C)-Cd(1)-S(1) 94.61(4)
N(1B)-Cd(1)-N(11) 89.53(6)	N(1A)-Cd(1)-S(1C) 86.60(5)
N(1A)-Cd(1)-N(11C) 89.53(6)	N(1B)-Cd(1)-S(1C) 93.40(5)
N(1B)-Cd(1)-N(11C) 90.47(6)	N(11)-Cd(1)-S(1C) 94.61(4)
N(11)-Cd(1)-N(11C) 180.000(1)	N(11C)-Cd(1)-S(1C) 85.39(4)
N(1A)-Cd(1)-S(1) 93.40(5)	S(1)-Cd(1)-S(1C) 180.000(11)
N(1B)-Cd(1)-S(1) 86.60(5)	

Symmetry transformations used to generate equivalent atoms:

A: -x, -y + 1, -z + 1; B: x + 1, y, z; C: -x + 1, -y + 1, -z + 1; D: x – 1, y, z; E: x, -y + 3/2, z.

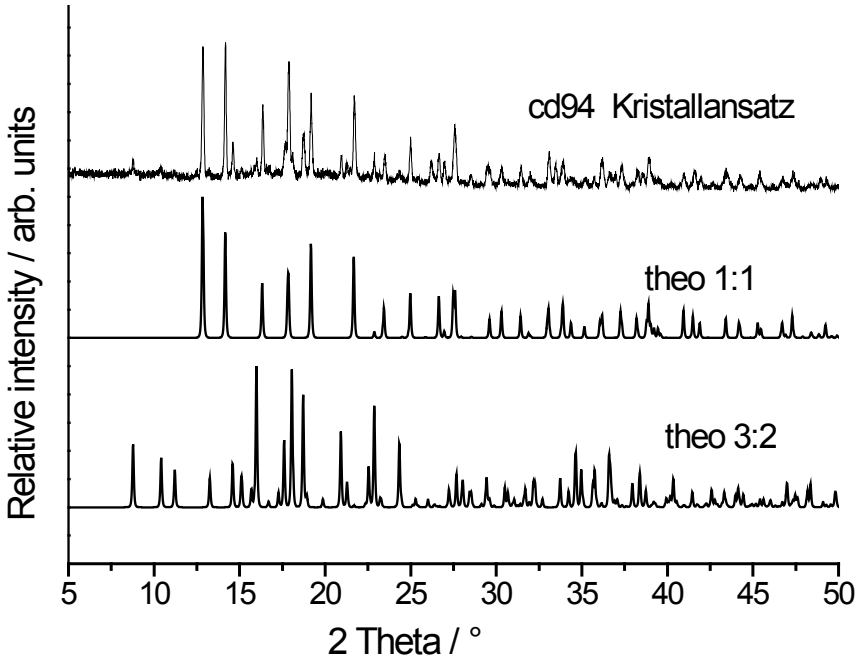

Figure S6. Experimental XRPD pattern of a mixture of single crystals of compound **1CI** and **1D** (top) and XRPD pattern for compound **1CI** (mid) and **1D** (bottom) calculated from single crystal data.

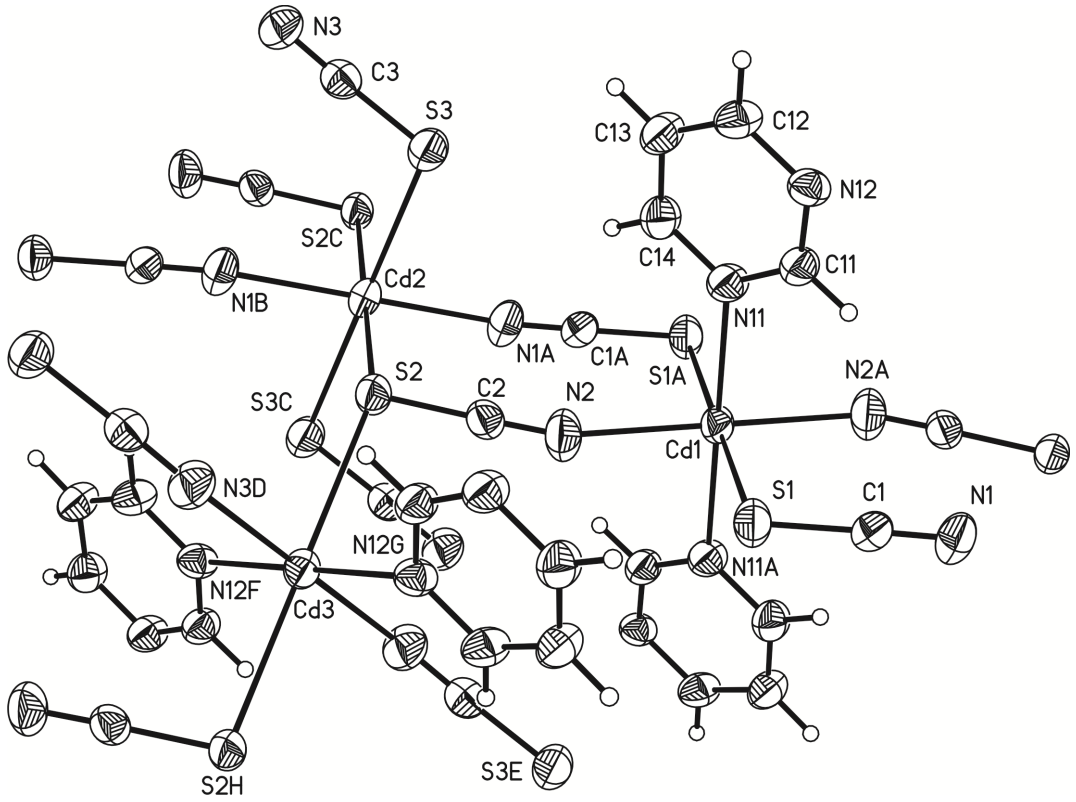

Figure S7. Crystal structure of compound **1D** with labeling and displacement ellipsoids drawn at the 50% probability level.

Table S4. Selected bond lengths [Å] and angles [°] for compound **1D**.

Cd(1)-N(2)	2.291(2)	Cd(1)-N(11A)	2.3542(17)
Cd(1)-N(2A)	2.291(2)	Cd(1)-S(1A)	2.7027(6)
Cd(1)-N(11)	2.3542(17)	Cd(1)-S(1)	2.7027(6)
N(2)-Cd(1)-N(2A)	180.000(1)	N(11)-Cd(1)-S(1A)	91.64(5)
N(2)-Cd(1)-N(11)	89.63(8)	N(11A)-Cd(1)-S(1A)	88.36(5)
N(2A)-Cd(1)-N(11)	90.37(8)	N(2)-Cd(1)-S(1)	86.44(6)
N(2)-Cd(1)-N(11A)	90.37(8)	N(2A)-Cd(1)-S(1)	93.56(6)
N(2A)-Cd(1)-N(11A)	89.63(8)	N(11)-Cd(1)-S(1)	88.36(5)
N(11)-Cd(1)-N(11A)	180.00(7)	N(11A)-Cd(1)-S(1)	91.64(5)
N(2)-Cd(1)-S(1A)	93.56(6)	S(1A)-Cd(1)-S(1)	180.00(2)
N(2A)-Cd(1)-S(1A)	86.44(6)		
Cd(2)-N(1A)	2.2499(19)	Cd(2)-S(3C)	2.7127(6)
Cd(2)-N(1B)	2.2499(19)	Cd(2)-S(2C)	2.7849(6)
Cd(2)-S(3)	2.7127(6)	Cd(2)-S(2)	2.7849(6)
N(1A)-Cd(2)-N(1B)	180.00(9)	S(3)-Cd(2)-S(2C)	91.95(2)
N(1A)-Cd(2)-S(3)	84.78(6)	S(3C)-Cd(2)-S(2C)	88.05(2)
N(1B)-Cd(2)-S(3)	95.22(6)	N(1A)-Cd(2)-S(2)	92.85(5)
N(1A)-Cd(2)-S(3C)	95.22(6)	N(1B)-Cd(2)-S(2)	87.15(5)
N(1B)-Cd(2)-S(3C)	84.78(6)	S(3)-Cd(2)-S(2)	88.05(2)
S(3)-Cd(2)-S(3C)	180.00(2)	S(3C)-Cd(2)-S(2)	91.95(2)
N(1A)-Cd(2)-S(2C)	87.15(5)	S(2C)-Cd(2)-S(2)	180.00(3)
N(1B)-Cd(2)-S(2C)	92.85(5)		
Cd(3)-N(3D)	2.271(2)	Cd(3)-N(12G)	2.3671(16)
Cd(3)-N(3E)	2.271(2)	Cd(3)-S(2)	2.7507(6)
Cd(3)-N(12F)	2.3671(16)	Cd(3)-S(2H)	2.7507(6)
N(3D)-Cd(3)-N(3E)	180.0	N(12F)-Cd(3)-S(2)	92.61(4)
N(3D)-Cd(3)-N(12F)	88.29(7)	N(12G)-Cd(3)-S(2)	87.39(4)
N(3E)-Cd(3)-N(12F)	91.71(7)	N(3D)-Cd(3)-S(2H)	95.99(6)
N(3D)-Cd(3)-N(12G)	91.71(7)	N(3E)-Cd(3)-S(2H)	84.01(6)
N(3E)-Cd(3)-N(12G)	88.29(7)	N(12F)-Cd(3)-S(2H)	87.39(4)
N(12F)-Cd(3)-N(12G)	180.00(5)	N(12G)-Cd(3)-S(2H)	92.61(4)
N(3D)-Cd(3)-S(2)	84.01(6)	S(2)-Cd(3)-S(2H)	180.0
N(3E)-Cd(3)-S(2)	95.99(6)		

Symmetry transformations used to generate equivalent atoms:

A: -x,-y+1,-z+1; B: x,y-1,z-1; C: -x,-y,-z; D: -x+1,-y,-z; E: x,y+1,z; F: x,y,z-1;
G: -x+1,-y+1,-z+1; H -x+1,-y+1,-z.

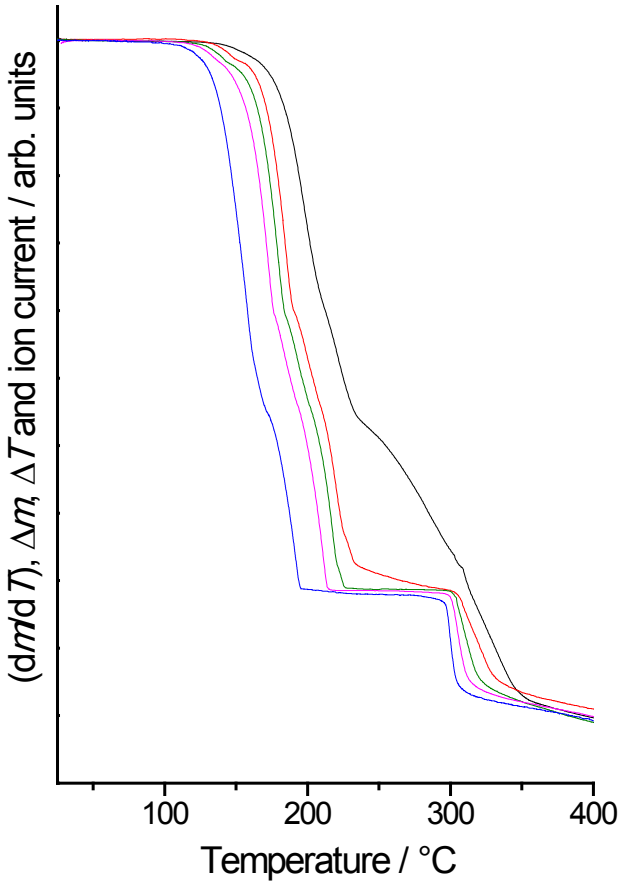

Fig. S8: Heating rate dependent measurements for compound **1A**.

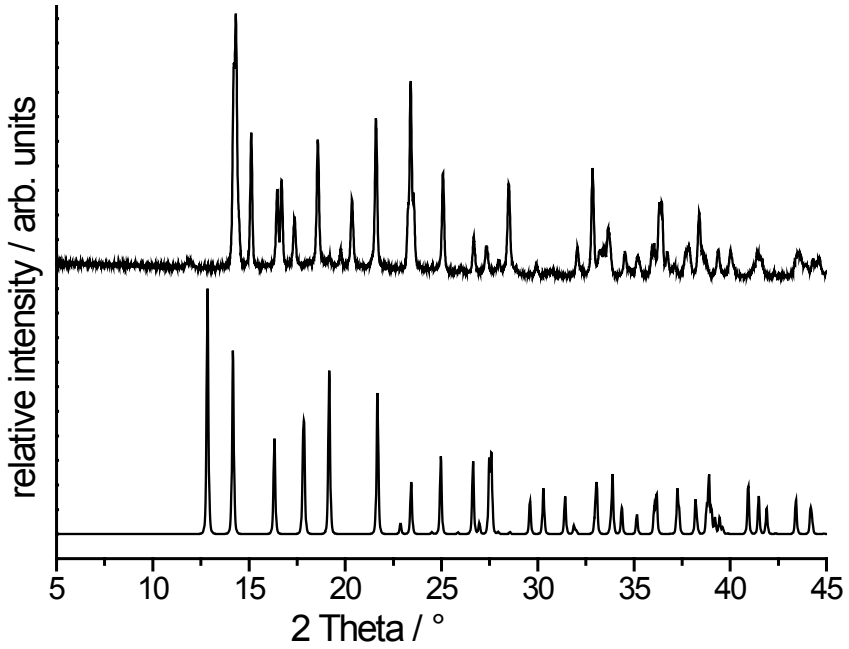

Fig. S9. XRPD pattern of the intermediate isolated in the thermal decomposition reaction of **1A** (top) and XRPD pattern of form **1CI** calculated from single crystal data (bottom).

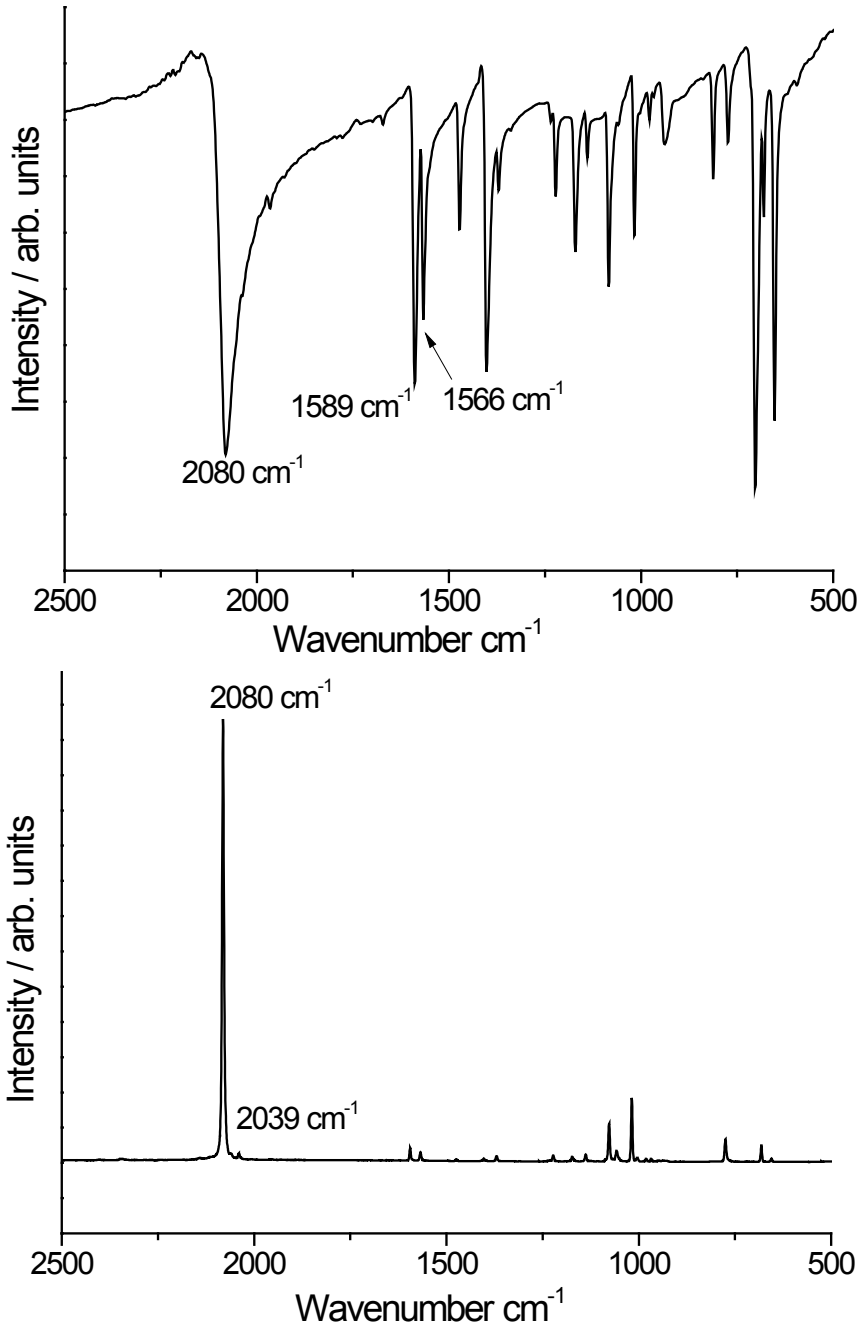

Fig. S10. IR (top) and Raman spectra (bottom) for compound **1CI**.

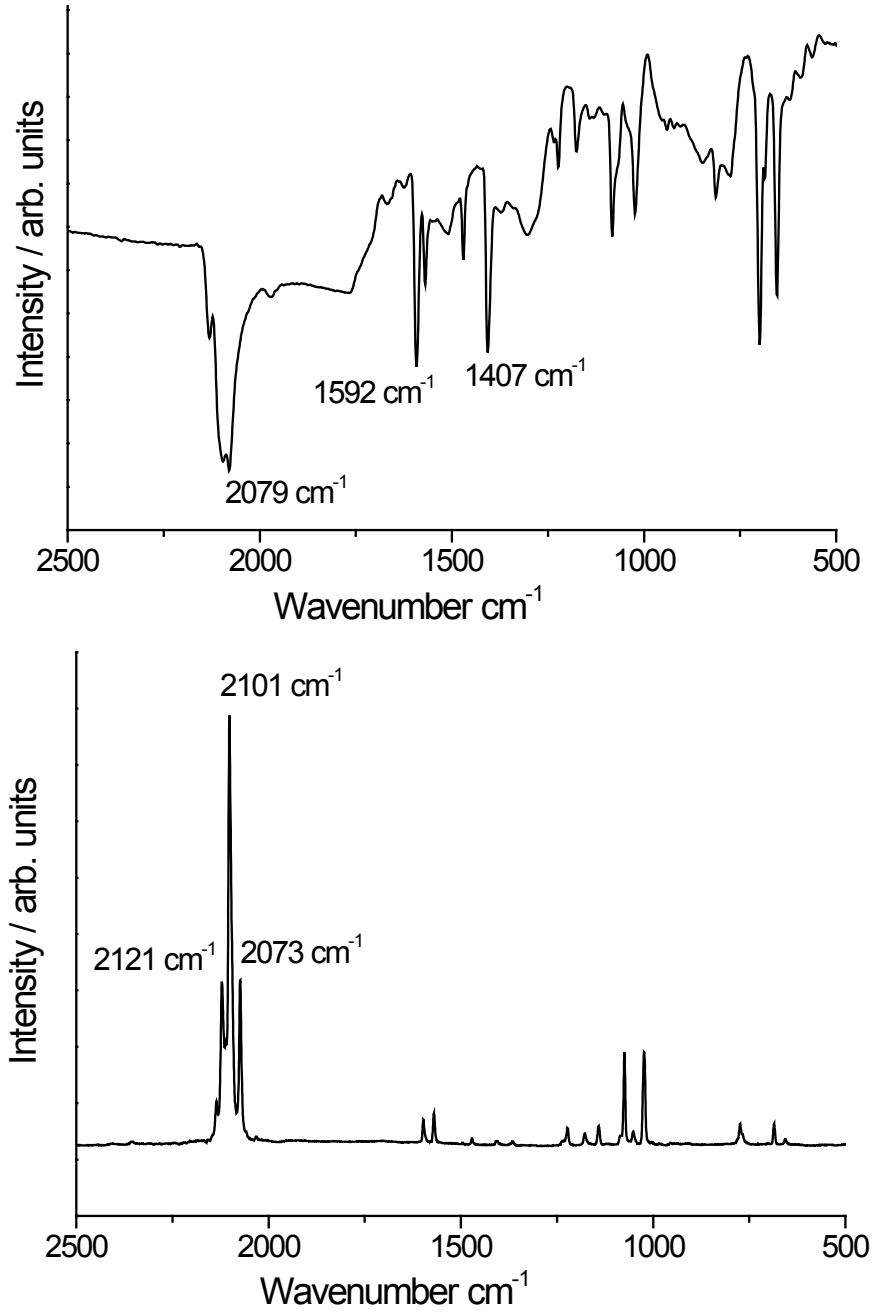

Fig. S11. IR (top) and Raman spectra (bottom) for compound **1CII**.

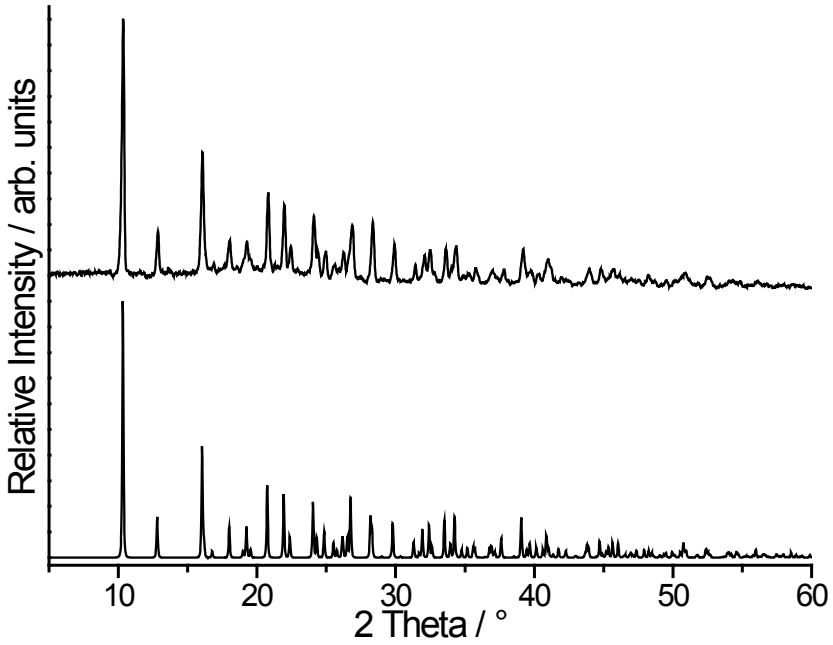

Fig. S12. Experimental and calculated XRPD pattern for compound **2A**.

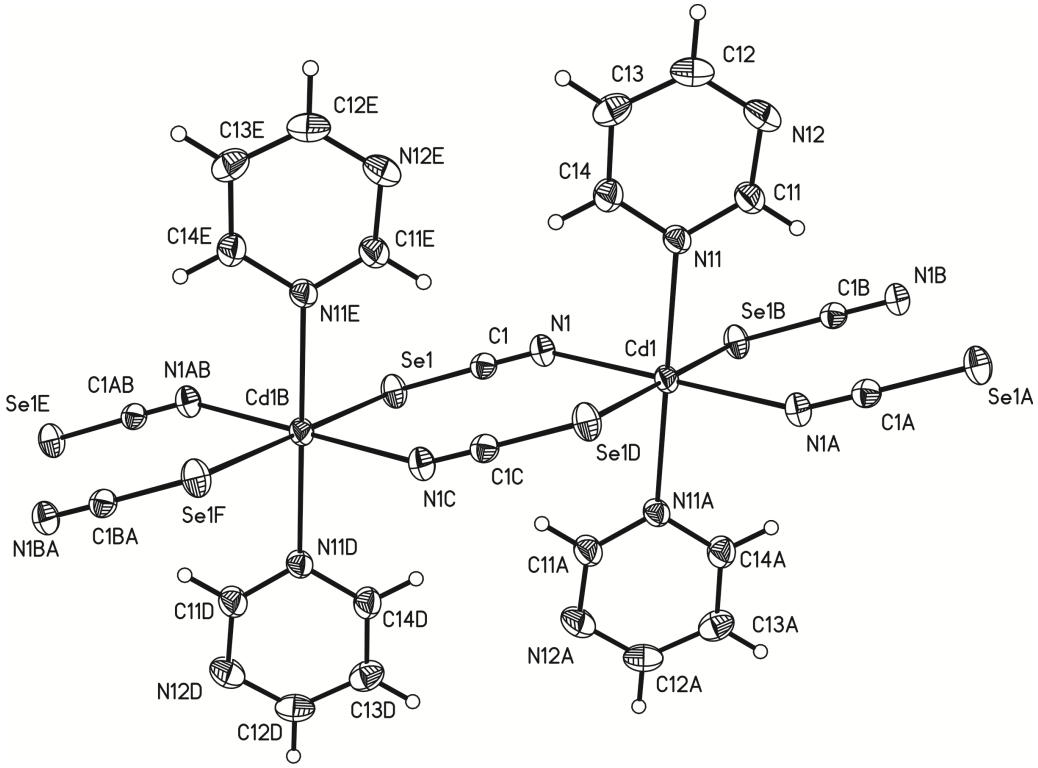

Fig. S13. Ortep plot of compound **2A**.

Table S5. Selected bond lengths [Å] and angles [°] for compound **2A**.

Cd(1)-N(1) 2.325(3)	Cd(1)-Se(1C) 2.8521(7)
Cd(1)-N(1A) 2.325(3)	Cd(1)-N(11) 2.368(3)
Cd(1)-Se(1B) 2.8521(7)	Cd(1)-N(11A) 2.368(3)
N(1)-Cd(1)-N(1A) 180.0	Se(1B)-Cd(1)-Se(1C) 180.0
N(1)-Cd(1)-Se(1B) 90.92(7)	N(1A)-Cd(1)-N(11) 90.02(11)
N(1A)-Cd(1)-Se(1B) 89.08(7)	N(1)-Cd(1)-N(11A) 90.02(11)
N(11)-Cd(1)-Se(1B) 87.24(7)	N(1A)-Cd(1)-N(11A) 89.98(11)
N(1)-Cd(1)-Se(1C) 89.08(7)	N(1)-Cd(1)-N(11) 89.98(11)
N(1A)-Cd(1)-Se(1C) 90.92(7)	N(11)-Cd(1)-N(11A) 180.0
N(11)-Cd(1)-Se(1C) 92.76(7)	N(11A)-Cd(1)-Se(1B) 92.76(7)
N(11A)-Cd(1)-Se(1C) 87.24(7)	C(13)-C(14) 1.369(6)

Symmetry transformations used to generate equivalent atoms:

A: -x, -y – 1, -z – 1; B: -x, -y – 2, -z – 1; C: x, y + 1, z; D: x, y – 1, z.

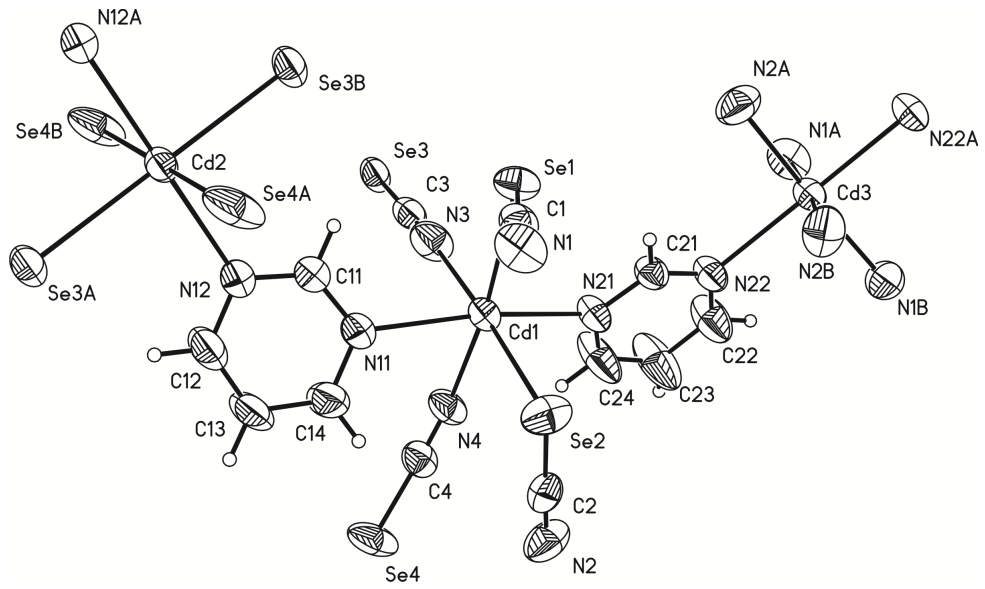

Fig. S14. Ortep plot of compound **2B**.

Table S6. Selected bond lengths [Å] and angles [°] for compound **2B**.

Cd(1)-N(3)	2.312(4)	Cd(1)-N(11)	2.442(4)
Cd(1)-N(4)	2.349(4)	Cd(1)-Se(2)	2.7298(6)
Cd(1)-N(21)	2.438(4)	Cd(1)-Se(1)	2.7538(5)
N(3)-Cd(1)-N(4)	84.28(15)	N(21)-Cd(1)-Se(2)	91.68(10)
N(3)-Cd(1)-N(21)	89.48(16)	N(11)-Cd(1)-Se(2)	91.62(10)
N(4)-Cd(1)-N(21)	85.53(13)	N(3)-Cd(1)-Se(1)	86.93(12)
N(3)-Cd(1)-N(11)	86.58(16)	N(4)-Cd(1)-Se(1)	171.08(10)
N(4)-Cd(1)-N(11)	82.83(14)	N(21)-Cd(1)-Se(1)	95.90(9)
N(21)-Cd(1)-N(11)	168.03(13)	N(11)-Cd(1)-Se(1)	95.18(10)
N(3)-Cd(1)-Se(2)	176.50(11)	Se(2)-Cd(1)-Se(1)	96.231(18)
N(4)-Cd(1)-Se(2)	92.52(10)		
Cd(2)-N(12A)	2.539(4)	Cd(2)-Se(4C)	2.7723(5)
Cd(2)-N(12)	2.539(4)	Cd(2)-Se(3D)	2.7918(4)
Cd(2)-Se(4B)	2.7723(5)	Cd(2)-Se(3E)	2.7918(4)
N(12A)-Cd(2)-N(12)	180.00(12)	Se(4B)-Cd(2)-Se(3D)	91.714(16)
N(12A)-Cd(2)-Se(4B)	94.30(11)	Se(4C)-Cd(2)-Se(3D)	88.285(16)
N(12)-Cd(2)-Se(4B)	85.70(11)	N(12A)-Cd(2)-Se(3E)	89.81(9)
N(12A)-Cd(2)-Se(4C)	85.70(11)	N(12)-Cd(2)-Se(3E)	90.19(9)
N(12)-Cd(2)-Se(4C)	94.30(11)	Se(4B)-Cd(2)-Se(3E)	88.286(16)
Se(4B)-Cd(2)-Se(4C)	180.0	Se(4C)-Cd(2)-Se(3E)	91.715(16)
N(12A)-Cd(2)-Se(3D)	90.19(9)	Se(3D)-Cd(2)-Se(3E)	180.000(18)
N(12)-Cd(2)-Se(3D)	89.81(9)		

Table S6. Selected bond lengths [Å] and angles [°] for compound **2B**.

Cd(3)-N(2F)	2.289(4)	Cd(3)-N(1I)	2.319(4)
Cd(3)-N(2G)	2.289(4)	Cd(3)-N(22J)	2.379(4)
Cd(3)-N(1H)	2.319(4)	Cd(3)-N(22)	2.379(4)
N(2F)-Cd(3)-N(2G)	82.8(3)	N(1H)-Cd(3)-N(22J)	89.96(15)
N(2F)-Cd(3)-N(1H)	176.11(18)	N(1I)-Cd(3)-N(22J)	90.72(15)
N(2G)-Cd(3)-N(1H)	94.23(18)	N(2F)-Cd(3)-N(22)	91.71(16)
N(2F)-Cd(3)-N(1I)	94.23(18)	N(2G)-Cd(3)-N(22)	87.57(16)
N(2G)-Cd(3)-N(1I)	176.11(17)	N(1H)-Cd(3)-N(22)	90.72(15)
N(1H)-Cd(3)-N(1I)	88.8(3)	N(1I)-Cd(3)-N(22)	89.96(15)
N(2F)-Cd(3)-N(22J)	87.57(16)	N(22J)-Cd(3)-N(22)	179.05(19)
N(2G)-Cd(3)-N(22J)	91.71(16)		

Symmetry transformations used to generate equivalent atoms:
A: -x+1, -y, -z+1; B: x-1/2, y-1/2, z; C: -x+3/2, -y+1/2, -z+1; D: x+1/2, y-1/2 ,z; E: -x+1/2, -y+1/2, -z+1; F: x-1, y, z; G: -x+1, y, -z+3/2; H: -x+1/2, y+1/2, -z+3/2; I: x-1/2, y+1/2, z; J: -x, y, -z+3/2; K: x+1, y, z; L: x+1/2, y+1/2, z.

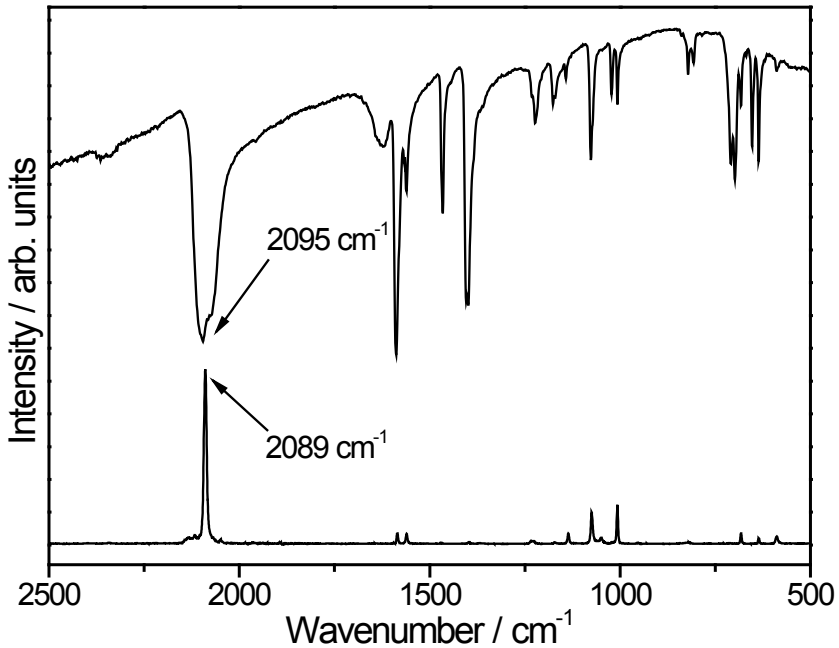

Fig. S15. IR (top) and Raman spectra (bottom) for compound **2A**.

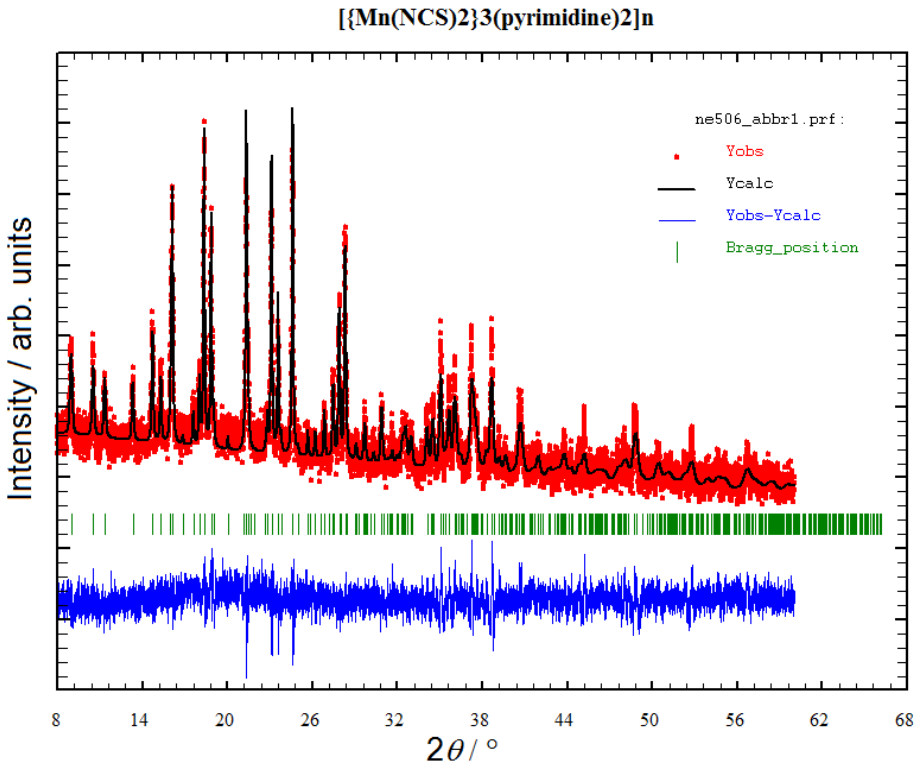

Fig. S16. Rietveld plot of the 3:2 compound $\{[Mn(NCS)_2]_3(pyrimidine)_2\}_n$.

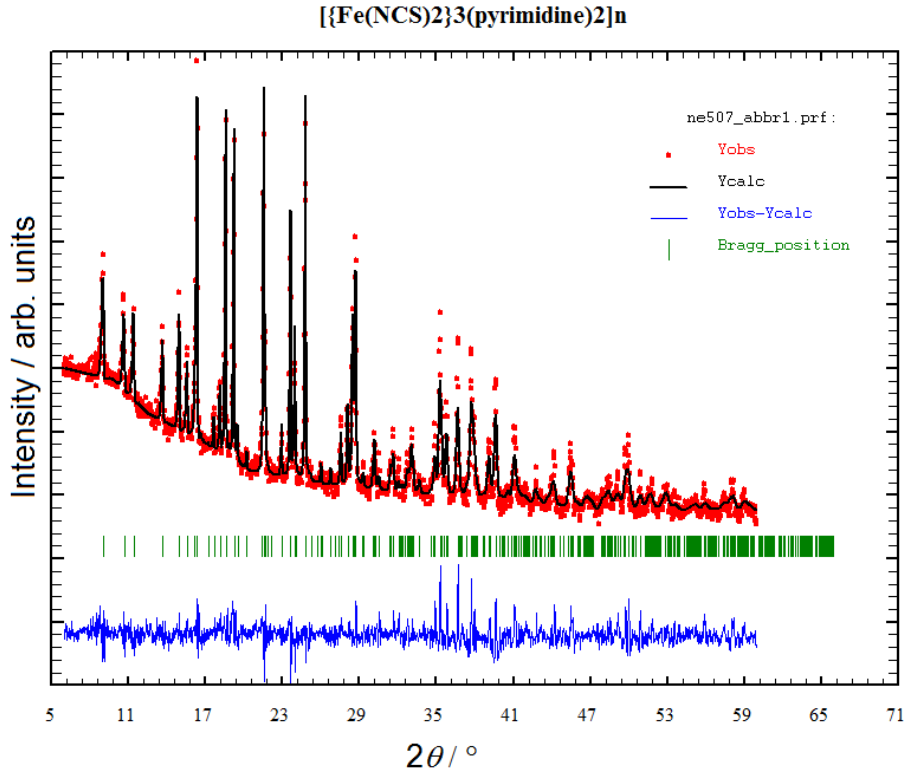

Fig. S17. Rietveld plot of the 3:2 compound $\{[Fe(NCS)_2]_3(pyrimidine)_2\}_n$.