Supplementary Information

Structure and Physical Properties of Substituted Malonate Divalent Metal Coordination Polymers with Dipyridylamine Co-Ligands: Acentric Chain, Herringbone Layer, and Novel Binodal Network Topologies

Gregory A. Farnum, Joseph A. Nettleman, Robert L. LaDuca*

Table S1. Selected Bond distance (Å) and angle (°) data for **1**.

Cu1–O1	1.946(2)	O1–Cu1–O3	89.49(10)
Cu1–O3	1.975(2)	O1–Cu1–O5	163.06(9)
Cu1–O5	1.979(2)	O3–Cu1–O5	90.02(9)
Cu1–N1	2.006(2)	O1–Cu1–N1	87.21(10)
Cu1–O6$^{\#1}$	2.190(2)	O3–Cu1–N1	171.58(10)
		O5–Cu1–N1	90.88(9)
		O1–Cu1–O6$^{\#1}$	101.72(9)
		O3–Cu1–O6$^{\#1}$	92.04(8)
		O5–Cu1–O6$^{\#1}$	95.22(8)
		N1–Cu1–O6$^{\#1}$	96.22(10)

Symmetry transformation to generate equivalent atoms: #1 x, $y + 1$, z.

Table S2. Hydrogen bonding distance (Å) and angle (°) data for **1**–**4**.

D–H···*A*	*d*(H···*A*)	<*D*H*A*	*d*(*D*···*A*)	symmetry transformation for *A*
1				
O1W–H1WA···O8	2.36(2)	139.1(18)	3.143(6)	
O1W–H1WB···O1	2.40	123.2	3.001(5)	$-x, -y + 2, z - 1/2$
O7–H7A···O4	1.85(2)	165(4)	2.705(3)	$x - 1/2, -y + 2, z$
N2–H2N···O2	1.86(2)	171(4)	2.732(4)	$x - 1/2, -y + 2, z$
N3–H3N···O4	1.88(5)	178(5)	2.694(4)	$-x, -y + 1, z + 1/2$
2				
N2–H2N···O5A	2.09(2)	173(3)	2.964(9)	$-x, y - 1, -z + 1/2$
N2–H2N···O7B	2.15(4)	178(4)	3.02(3)	$-x, y - 1, -z + 1/2$
N5–H5N···O5A	2.484(13)	122.7(4)	3.049(9)	$x + 1/2, -y + 1/2, z + 1/2$
3				
N2–H2N···O11	2.12(2)	178(6)	3.000(7)	$x + 1/2, -y + 1/2, z - 1/2$
N5–H5N···O14	1.92(3)	172(12)	2.804(7)	
N4–H4N···O2	1.81(3)	171(12)	2.699(6)	$-x + 3/2, y + 1/2, -z + 1/2$
O14–H14O···O2W	1.84(3)	172(12)	2.716(8)	$x + 1, y, z$
4				
N2–H2N···O1W	2.13	169.3	2.9881(18)	$x - 1/2, y + 1/2, z$
N3–H3N···O3	1.79	175.4	2.6718(16)	$x, -y + 2, z + 1/2$
O2W–H2WA···O3W	1.94	159.0	2.816(2)	$-x + 1/2, -y + 5/2, -z + 1$
O2W–H2WB···O2	1.98	163.6	2.7944(18)	$-x + 1/2, -y + 3/2, -z + 1$
O1W–H1WA···O2	1.93	167.6	2.7457(16)	
O1W–H1WB···O4	1.95	156.8	2.7551(16)	$-x + 1/2, y + 1/2, -z + 1/2$
O3W–H3WA···O1W	2.04	166.9	2.8710(18)	
O3W–H3WB···O2W	1.91	161.6	2.746(2)	

Table S3. Selected Bond distance (Å) and angle (°) data for **2**.

Cu1–O1$^{\#1}$	1.962(2)	O1$^{\#1}$–Cu1–O4	177.79(8)
Cu1–O4	1.9900(19)	O1$^{\#1}$–Cu1–N3	93.48(9)
Cu1–N3	1.993(2)	O4–Cu1–N3	87.73(9)
Cu1–N1$^{\#2}$	2.004(2)	O1$^{\#1}$–Cu1–N1$^{\#2}$	91.72(9)
Cu1–O2	2.199(2)	O4–Cu1–N1$^{\#2}$	86.70(9)
Cu2–O3	1.9617(19)	N3–Cu1–N1$^{\#2}$	166.41(10)
Cu2–N4	2.027(2)	O1$^{\#1}$–Cu1–O2	96.06(8)
		O4–Cu1–O2	85.69(8)
		N3–Cu1–O2	93.95(9)
		N1$^{\#2}$–Cu1–O2	97.98(9)
		O3$^{\#3}$–Cu2–O3	180.0
		O3$^{\#3}$–Cu2–N4	89.68(9)
		O3–Cu2–N4	90.33(9)
		N4–Cu2–N4$^{\#3}$	180.0

Symmetry transformation to generate equivalent atoms: #1 $-x + 1/2, y - 1/2, -z + 1/2$; #2 $x + 1/2, -y - 1/2, z + 1/2$; #3 $-x + 1/2, -y - 1/2, -z + 1$.

Table S4. Selected Bond distance (Å) and angle (°) data for **3**.

Cd1–O5$^{\#1}$	2.195(4)	N1–Cd1–O3	88.93(13)
Cd1–N1	2.256(4)	O4–Cd1–O3	54.94(11)
Cd1–O4	2.343(3)	O1–Cd1–O3	115.47(12)
Cd1–O1	2.380(4)	O2–Cd1–O3	88.42(12)
Cd1–O2	2.397(4)	O6$^{\#1}$–Cd2–N3$^{\#2}$	89.70(16)
Cd1–O3	2.430(4)	O6$^{\#1}$–Cd2–N6	84.85(16)
Cd2–O6$^{\#1}$	2.272(4)	N3$^{\#2}$–Cd2–N6	171.94(15)
Cd2–N3$^{\#2}$	2.297(4)	O6$^{\#1}$–Cd2–O8$^{\#3}$	133.31(14)
Cd2–N6	2.311(4)	N3$^{\#2}$–Cd2–O8$^{\#3}$	88.34(15)
Cd2–O8$^{\#3}$	2.315(4)	N6–Cd2–O8$^{\#3}$	91.08(15)
Cd2–O8	2.320(4)	O6$^{\#1}$–Cd2–O8	154.29(15)
Cd2–O4	2.503(4)	N3$^{\#2}$–Cd2–O8	101.00(15)
Cd2–O7$^{\#3}$	2.744(4)	N6–Cd2–O8	86.38(15)
O5$^{\#1}$–Cd1–N1	106.15(17)	O8–Cd2–O8$^{\#3}$	70.91(14)
O5$^{\#1}$–Cd1–O4	99.10(14)	O6$^{\#1}$–Cd2–O4	85.46(13)
N1–Cd1–O4	126.63(14)	N3$^{\#2}$–Cd2–O4	89.05(14)
O5$^{\#1}$–Cd1–O1	87.48(14)	N6–Cd2–O4	96.42(14)
N1–Cd1–O1	86.79(14)	O8$^{\#3}$–Cd2–O4	141.11(12)
O4–Cd1–O1	141.25(12)	O8–Cd2–O4	71.56(11)
O5$^{\#1}$–Cd1–O2	95.38(15)	O6$^{\#1}$–Cd2–O7$^{\#3}$	82.72(13)
N1–Cd1–O2	135.01(14)	N3$^{\#2}$–Cd2–O7$^{\#3}$	88.55(14)
O4–Cd1–O2	86.63(12)	N6–Cd2–O7$^{\#3}$	84.88(14)
O1–Cd1–O2	54.67(12)	O8$^{\#3}$–Cd2–O7$^{\#3}$	50.60(12)
O5$^{\#1}$–Cd1–O3	153.57(14)	O8–Cd2–O7$^{\#3}$	120.50(12)
		O4–Cd2–O7$^{\#3}$	167.95(11)

Symmetry transformation to generate equivalent atoms: #1 $-x+1, -y, -z$; #2 $-x+3/2, y-1/2, -z+1/2$; #3 $-x+2, -y, -z+1$.

Table S5. Selected Bond distance (Å) and angle (°) data for **4**.

Co1–O1	2.0716(10)	O1–Co1–O1$^{\#1}$	176.16(6)
Co1–O3	2.1195(10)	O1–Co1–O3	84.49(4)
Co1–N1	2.1522(12)	O1$^{\#1}$–Co1–O3	92.95(4)
		O3$^{\#1}$–Co1–O3	97.01(6)
		O1–Co1–N1	87.16(4)
		O1$^{\#1}$–Co1–N1	95.56(4)
		O3$^{\#1}$–Co1–N1	87.17(4)
		O3–Co1–N1	170.84(4)
		N1–Co1–N1$^{\#1}$	89.88(7)

Symmetry transformation to generate equivalent atoms: #1 $-x, y, -z + 1/2$.

Figure S1. Supramolecular layer of **1**. Hydrogen bonding is indicated as dashed bars.

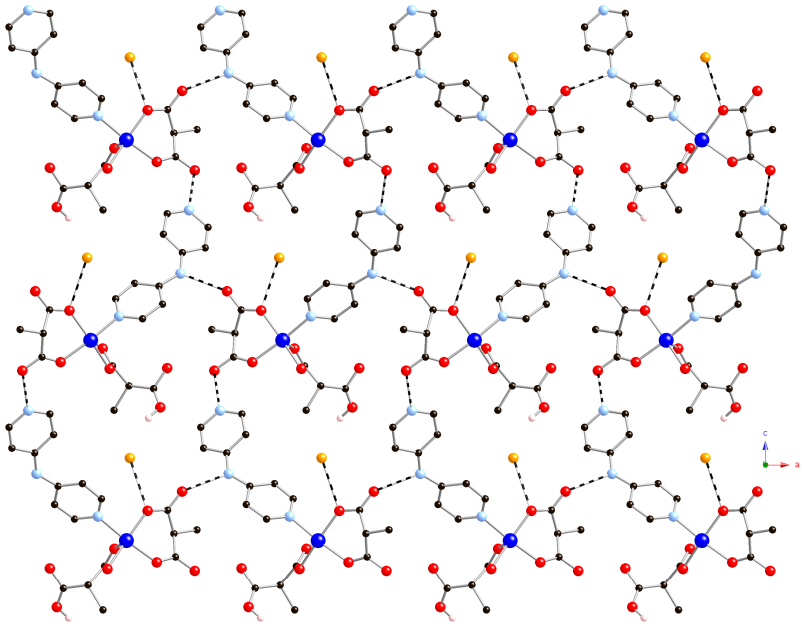


Figure S2. Stacking diagram of **3**, showing unligated species between the (6,3) layers.

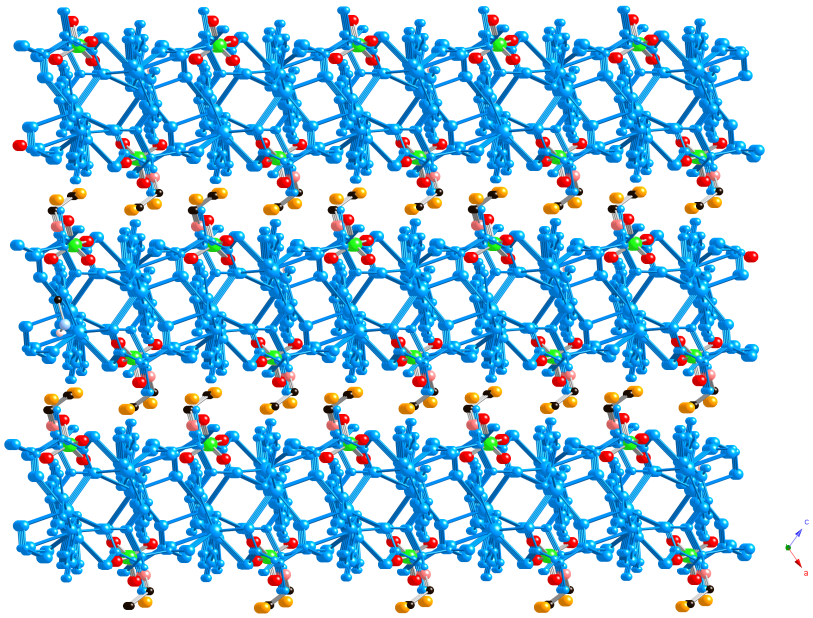


Figure S3. Supramolecular ribbon motifs in **4**. Hydrogen bonding is indicated as dashed bars.

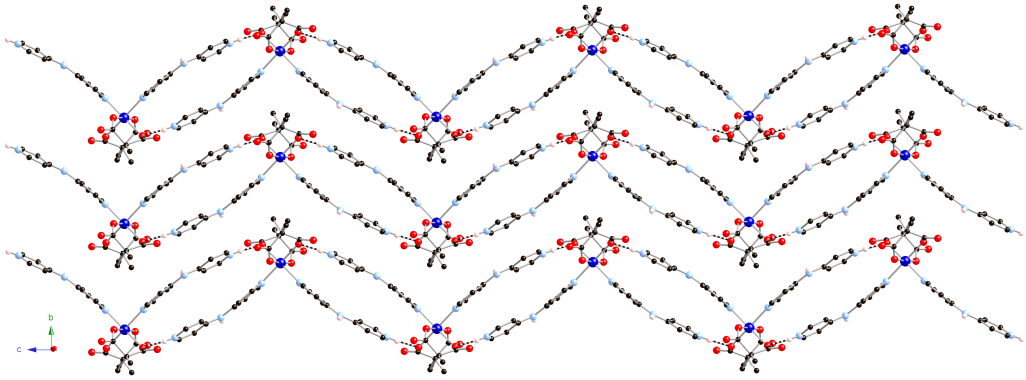


Figure S4. Curie-Weiss plot for **1**.

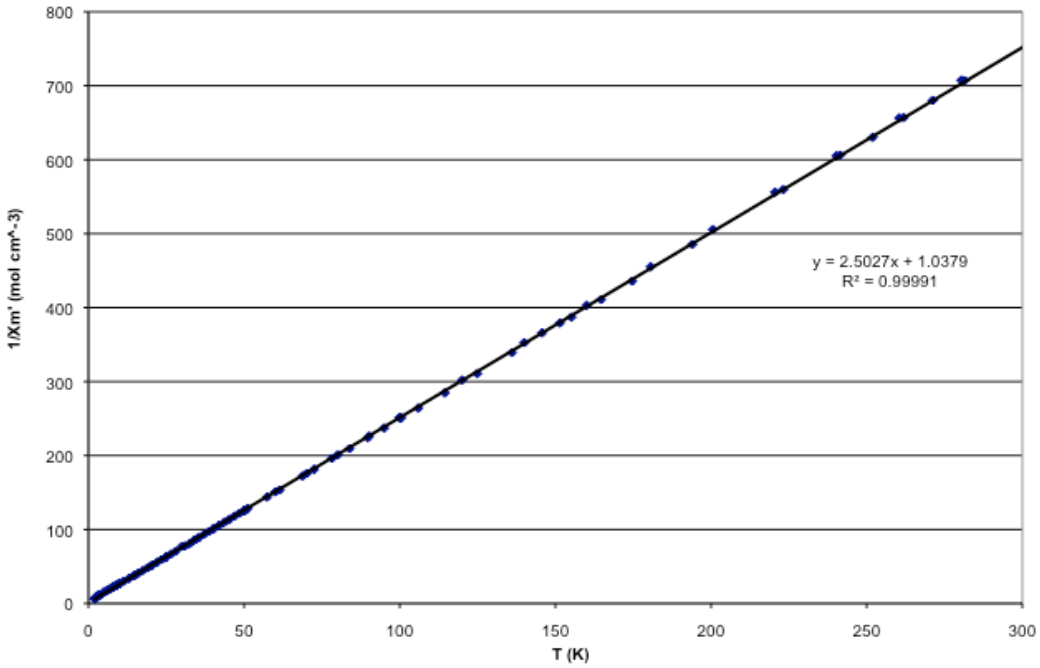


Figure S5. Curie-Weiss plot for **2**.

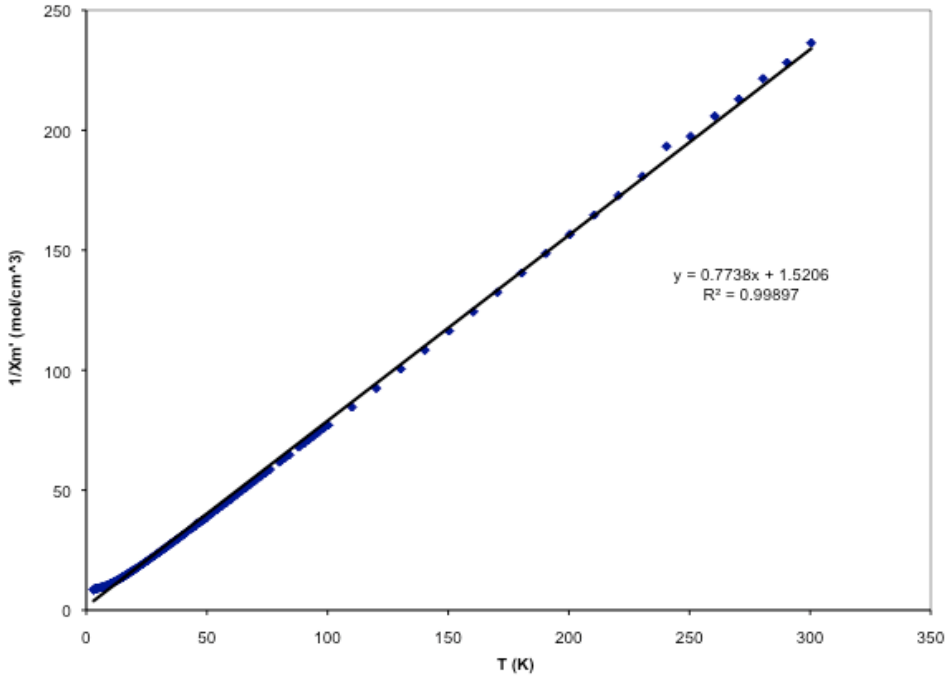


Figure 6. PXRD spectrum of **1**. The thin lines represent the calculated pattern.

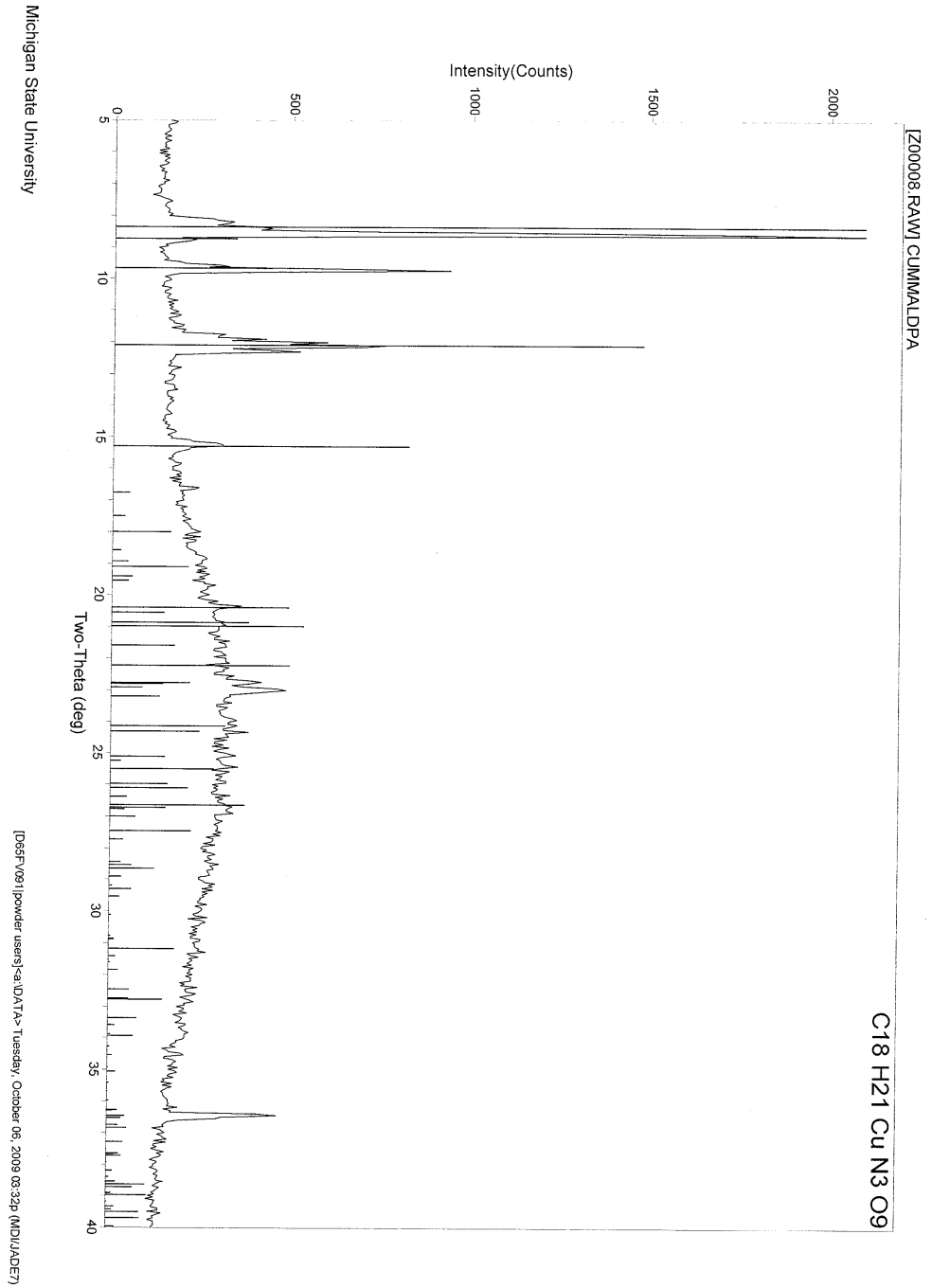


Figure 7. PXRD spectrum of **2**. The thin lines represent the calculated pattern.

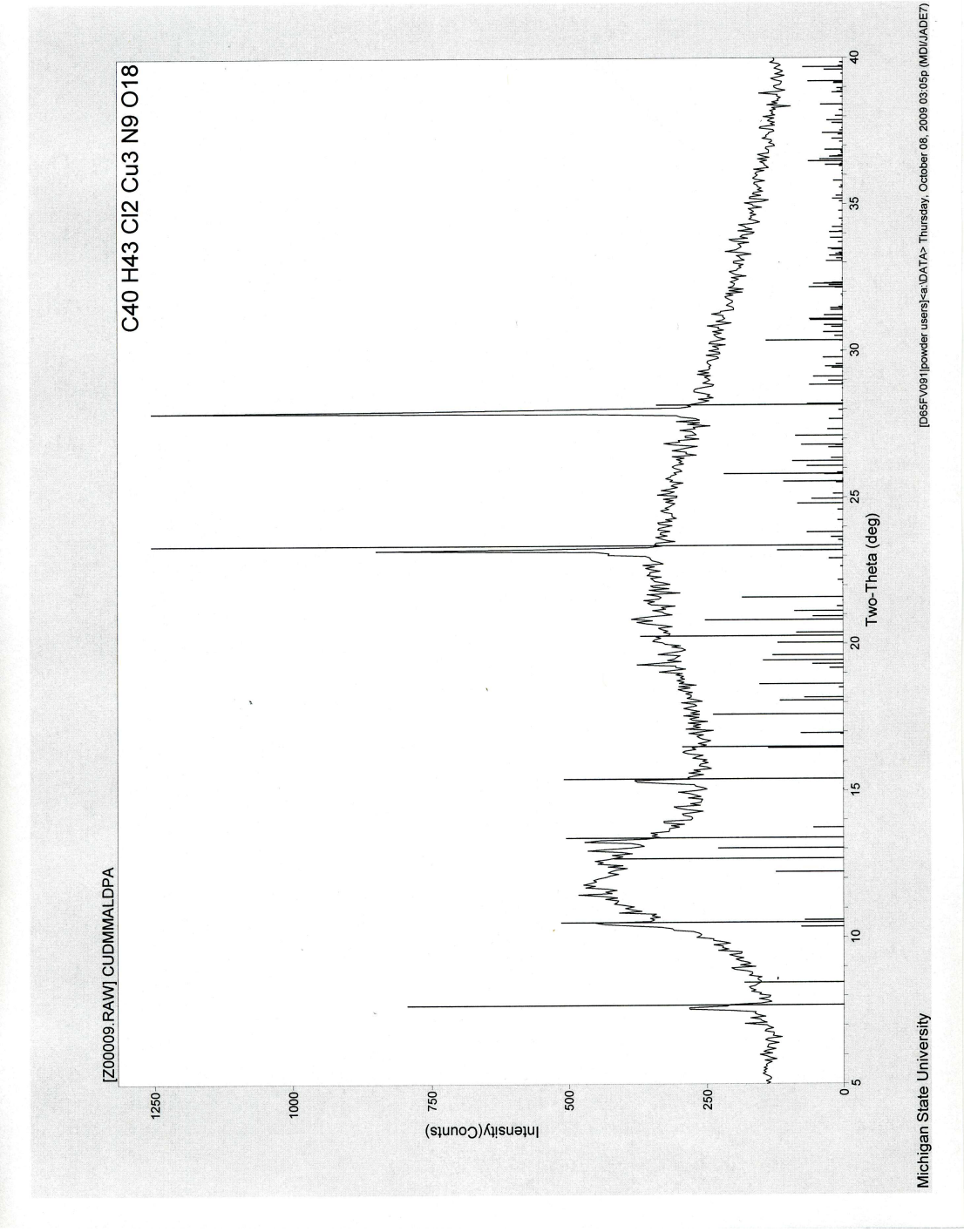
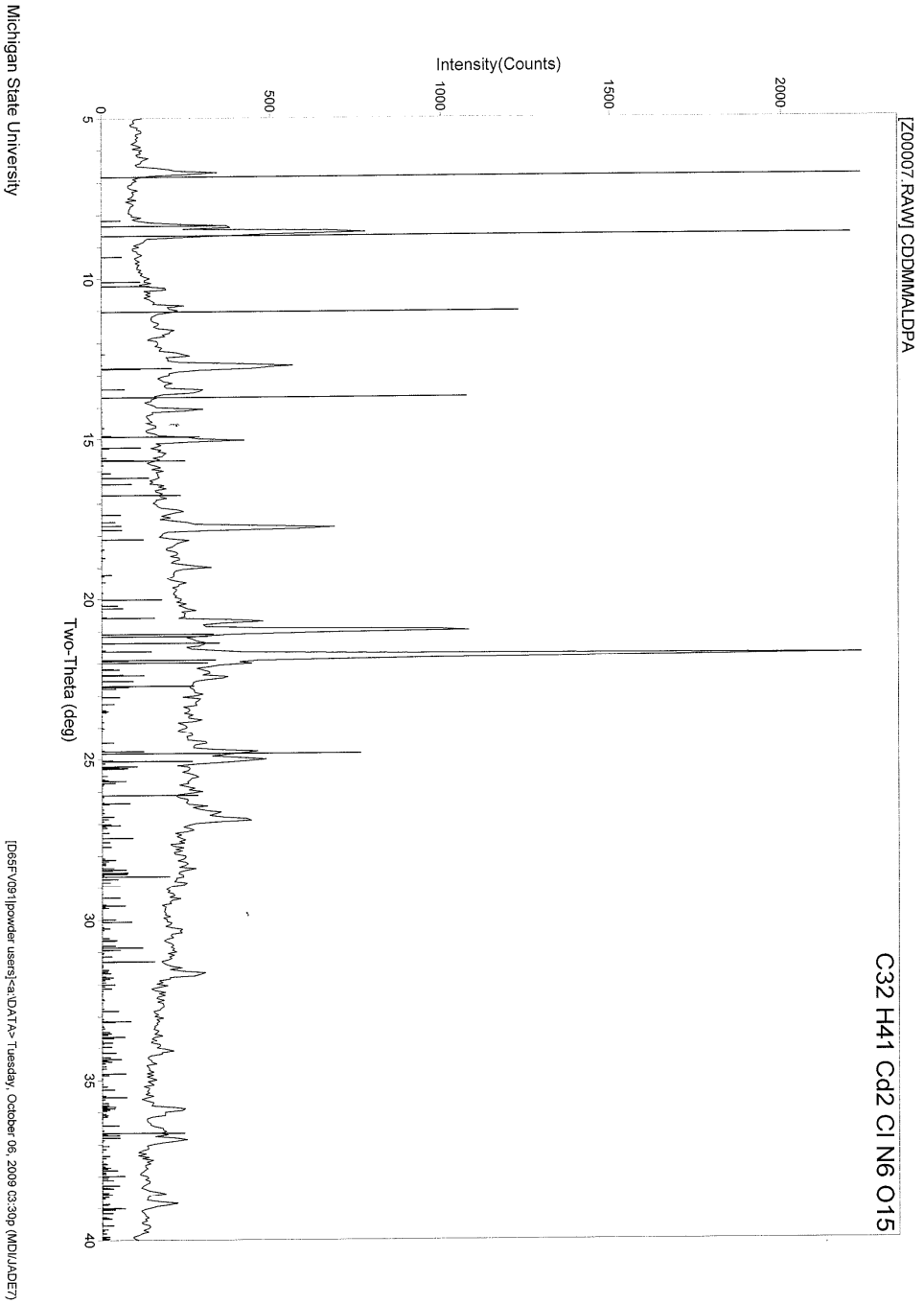


Figure 8. PXRD spectrum of **3**. The thin lines represent the calculated pattern.



Supplementary Material (ESI) for CrystEngComm