Supplementary Information

CuN_6 Jahn–Teller centers in coordination frameworks comprising fully condensed Kuratowski–type secondary building units: phase transitions and magneto–structural correlations

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Table S1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **α**–[Cu(ta)$_2$]. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	**x**	**y**	**z**	**U(eq)**
Cu2	0	7500	1250	15(1)
Cu1	0	5000	0	20(1)
N4	0	7500	13(3)	20(2)
N2	1218(3)	6282(3)	1250	26(1)
N3	0	3415(4)	394(2)	23(1)
N1	1284(3)	5447(3)	779(2)	35(1)
C1	0	3070(5)	1062(3)	36(2)
C2	2194(4)	4835(4)	961(3)	52(2)

Table S2. Bond lengths [Å] and angles [deg] for **α**–[Cu(ta)$_2$].

Cu2-N2	2.040(4)	Cu1-N1#6	2.186(4)
Cu2-N2#1	2.040(4)	N4-N3#4	1.330(5)
Cu2-N2#2	2.040(4)	N4-N3#7	1.330(5)
Cu2-N2#3	2.040(4)	N2-N1#8	1.336(4)
Cu2-N4#2	2.348(6)	N2-N1	1.336(4)
Cu2-N4	2.348(6)	N3-N4#4	1.330(5)
Cu1-N3#4	2.021(5)	N3-C1	1.333(7)
Cu1-N3	2.021(5)	N1-C2	1.343(6)
Cu1-N1	2.186(4)	C1-C1#9	1.351(12)
Cu1-N1#4	2.186(4)	C2-C2#8	1.352(11)
Cu1-N1#5	2.186(4)		

N(2)-Cu(2)-N(2)#1	90.0	N(3)#4-Cu(1)-N(1)#6	88.57(13)
N(2)-Cu(2)-N(2)#2	90.0	N(3)-Cu(1)-N(1)#6	91.43(13)
N(2)#1-Cu(2)-N(2)#2	180.0	N(1)#4-Cu(1)-N(1)#6	88.20(19)
N(2)-Cu(2)-N(2)#3	180.0	N(1)#5-Cu(1)-N(1)#6	180.00(15)
N(2)#1-Cu(2)-N(2)#3	90.0	N(3)#4-Cu(1)-N(1)	91.43(13)
N(2)#2-Cu(2)-N(2)#3	90.0	N(3)-Cu(1)-N(1)	88.57(13)
N(2)-Cu(2)-N(4)#2	90.0	N(1)#4-Cu(1)-N(1)	180.0
N(2)#1-Cu(2)-N(4)#2	90.0	N(1)#5-Cu(1)-N(1)	88.20(19)
N(2)#2-Cu(2)-N(4)#2	90.0	N(1)#6-Cu(1)-N(1)	91.80(19)
N(2)#3-Cu(2)-N(4)#2	90.0	N(3)#4-N(4)-N(3)#7	109.1(6)
N(2)-Cu(2)-N(4)	90.0	N(3)#4-N(4)-Cu(2)	125.4(3)
N(2)#1-Cu(2)-N(4)	90.0	N(3)#7-N(4)-Cu(2)	125.4(3)
N(2)#2-Cu(2)-N(4)	90.0	N(1)#8-N(2)-N(1)	111.2(5)
N(2)#3-Cu(2)-N(4)	90.0	N(1)#8-N(2)-Cu(2)	124.4(2)
N(1)#2-Cu(2)-N(4)	180.0	N(1)-N(2)-Cu(2)	124.4(2)
N(3)#4-Cu(1)-N(3)	180.0	N(4)#4-N(3)-C(1)	107.6(5)
N(3)#4-Cu(1)-N(1)#4	88.57(13)	N(4)#4-N(3)-Cu(1)	122.9(4)
N(3)-Cu(1)-N(1)#4	91.43(13)	C(1)-N(3)-Cu(1)	129.5(4)
N(3)#4-Cu(1)-N(1)#5	91.43(13)	N(2)-N(1)-C(2)	105.9(4)
N(3)-Cu(1)-N(1)#5	88.57(13)	N(2)-N(1)-Cu(1)	126.2(3)
N(4)#4-Cu(1)-N(1)#5	91.80(19)	C(2)-N(1)-Cu(1)	127.0(3)
N(3)-C(1)-C(1)#9	107.8(3)	N(1)-C(2)-C(2)#8	108.5(3)

Symmetry transformations used to generate equivalent atoms:

#1 -y+3/4,x+3/4,-z+1/4; #2 y-3/4,-x+3/4,-z+1/4; #3 -x+0,-y+3/2,z+0; #4 -x,-y+1,-z; #5 -x,y,z; #6 x,-y+1,-z; #7 x,y+1/2,-z; #8 -y+3/4,-x+3/4,-z+1/4; #9 -x+0,-y+1/2,z+0

Table S3. Atomic coordinates and equivalent isotropic displacement parameters for **β**–[Cu(ta)$_2$].

Atom	**x**	**y**	**z**	**U**
Cu1	0	0.5	0	0.056(2)
Cu2	0.125	0.625	0.125	0.047(3)
C1	0.0977(3)	0.3758(4)	0.0977(3)	0.047(5)
N1	0.08042(10)	0.4489(3)	0.08042(10)	0.066(4)
N2	0.125	0.4922(5)	0.125	0.039(5)
H1	0.075616	0.332552	0.075616	0.038 96

Table S4. Selected bond distances [Å] and bond angles [deg] for **β**–[Cu(ta)$_2$].

C1-C1^{i}	1.349(7)	Cu2-N2	2.317(9)
C1-N1	1.344(8)	Cu2-N2^{ix}	2.317(9)
C1-N1^{i}	2.185(7)	Cu2-N2^{ii}	2.317(9)
C1-N2	2.139(11)	Cu2-N2^{x}	2.317(9)
Cu1-N1	2.174(3)	Cu2-N2^{iii}	2.317(9)
Cu1-N1^{ii}	2.174(3)	Cu2-N2^{xi}	2.317(9)
Cu1-N1^{iii}	2.174(3)	N1-N1^{i}	2.199(2)
Cu1-N1^{iv}	2.174(3)	N1-N1^{iv}	2.897(3)
Cu1-N1^{v}	2.174(3)	N1-N1^{v}	2.897(3)
Cu1-N1^{vi}	2.174(3)	N1-N2	1.334(6)

C1^{i}-C1-N1;	108.4(5)	N2^{iii}-Cu1-N2^{iv}	180.0(5)	C1^{i}-N1-N1^{iv}	123.7(2)
C1^{i}-C1-N2	71.6(4)	N2^{iii}-Cu1-N2^{vii}	115.88(18)	C1^{i}-N1-N1^{v}	123.7(2)
N1-C1-N1^{i}	72.7(3)	N2^{iii}-Cu1-N2^{viii}	115.88(18)	C1^{i}-N1-N2	70.2(4)
N1-Cu1-N1^{ii}	96.46(13)	N2^{iv}-Cu1-N2^{vii}	64.12(18)	Cu1-N1-N1^{i}	155.8(3)
N1-Cu1-N1^{iii}	96.46(13)	N1^{iii}-Cu1-N2^{vii}	97.91(15)	Cu1-N1-N1^{iv}	48.23(9)
N1-Cu1-N1^{iv}	83.54(13)	N2^{iv}-Cu1-N2^{viii}	64.12(18)	Cu1-N1-N1^{v}	48.23(9)
N1-Cu1-N1^{v}	83.54(13)	N2^{vii}-Cu1-N2^{viii}	64.12(18)	Cu1-N1-N2	121.4(4)
N1-Cu1-N1^{vi}	180.0(5)	N2-Cu2-N2^{ix}	180.0(5)	N1^{i}-N1-N1^{iv}	144.05(15)
N1-Cu1-N2^{ii}	82.09(15)	N2-Cu2-N2^{ii}	90	N1^{i}-N1-N1^{v}	144.05(15)
N1-Cu1-N2^{ii}	82.09(15)	N2-Cu2-N2^{x}	90	N1^{iv}-N1-N1^{v}	68.09(15)
N1-Cu1-N2^{iv}	97.91(15)	N2-Cu2-N2^{iii}	90	N1^{iv}-N1-N2	140.1(2)
N1-Cu1-N2^{vii}	97.91(15)	N2-Cu2-N2^{xi}	90	N1^{v}-N1-N2	140.1(2)
N1-Cu1-N2^{viii}	158.3(2)	N2^{ix}-Cu2-N2^{ii}	90	C1-N2-Cu1	74.16(17)
N1^{ii}-Cu1-N1^{iii}	96.46(13)	N2^{ix}-Cu2-N2^{x}	90	C1-N2-Cu1^{i}	110.9(3)
N1^{ii}-Cu1-N1^{iv}	83.54(13)	N2^{ix}-Cu2-N2^{iii}	90	C1-N2-Cu2	161.62(16)
N1^{ii}-Cu1-N1^{v}	180.0(5)	N2^{ix}-Cu2-N2^{xi}	90	C1-N2-N1^{i}	73.9(5)
N1^{ii}-Cu1-N1^{vi}	83.54(13)	N2^{ii}-Cu2-N2^{x}	180.0(5)	C1^{i}-N2-Cu1	110.9(3)
N1^{ii}-Cu1-N2	82.09(15)	N2^{ii}-Cu2-N2^{iii}	90	C1^{i}-N2-Cu1^{i}	74.16(17)
N1^{ii}-Cu1-N2^{iii}	82.09(15)	N2^{ii}-Cu2-N2^{xi}	90	C1^{i}-N2-Cu2	161.62(16)
N1^{ii}-Cu1-N2^{iv}	97.91(15)	N2^{x}-Cu2-N2^{iii}	90	C1^{i}-N2-N1	73.9(5)
N1^{ii}-Cu1-N2^{vii}	158.3(2)	N2^{x}-Cu2-N2^{xi}	90	Cu1-N2-Cu1^{i}	174.9(3)
N1^{ii}-Cu1-N2^{viii}	97.91(15)	N2^{iii}-Cu2-N2^{xi}	180.0(5)	Cu1-N2-Cu2	87.46(16)
N1^{iii}-Cu1-N1^{iv}	180.0(5)	C1-N1-Cu1	132.6(3)	Cu1-N2-N1^{i}	148.1(5)
N1^{iii}-Cu1-N1^{v}	83.54(13)	C1-N1-N1^{i}	71.6(3)	Cu1^{i}-N2-Cu2	87.46(16)
N1^{iii}-Cu1-N1^{vi}	83.54(13)	C1-N1-N1^{iv}	95.1(3)	Cu1^{i}-N2-N1	148.1(5)
N1^{iii}-Cu1-N2	82.09(15)	C1-N1-N1^{v}	95.1(3)	Cu2-N2-N1	124.4(4)
N1^{iii}-Cu1-N2^{ii}	82.09(15)	C1-N1-N2	106.0(4)	Cu2-N2-N1^{i}	124.4(4)
N1^{iii}-Cu1-N2^{iv}	158.3(2)	C1^{i}-N1-Cu1	168.5(3)	N1-N2-N1^{i}	111.1(7)
N1^{iii}-Cu1-N2^{viii}	97.91(15)	N1^{iv}-Cu1-N1^{v}	96.46(13)	N1^{iv}-Cu1-N1^{vi}	96.46(13)
N1^{iv}-Cu1-N2	97.91(15)	N1^{iv}-Cu1-N2^{ii}	97.91(15)	N1^{iv}-Cu1-N2^{iii}	158.3(2)
N1^{iv}-Cu1-N2^{vii}	82.09(15)	N1^{iv}-Cu1-N2^{viii}	82.09(15)	N1^{v}-Cu1-N1^{vi}	96.46(13)
N1^{v}-Cu1-N2	97.91(15)	N1^{v}-Cu1-N2^{ii}	158.3(2)	N1v-Cu1-N2^{iii}	97.91(15)
N1^{v}-Cu1-N2^{iv}	82.09(15)	N1^{v}-Cu1-N2^{viii}	82.09(15)	N1^{vi}-Cu1-N2	158.3(2)
N1^{vi}-Cu1-N2^{ii}	97.91(15)	N1^{vi}-Cu1-N2^{iii}	97.91(15)	N1^{vi}-Cu1-N2^{iv}	82.09(15)
N1^{vi}-Cu1-N2^{vii}	82.09(15)	N2-Cu1-N2^{ii}	64.12(18)	N2-Cu1-N2^{iii}	64.12(18)
N2-Cu1-N2^{iv}	115.88(18)	N2-Cu1-N2^{vii}	115.88(18)	N2-Cu1-N2^{viii}	180.0(5)
N2^{ii}-Cu1-N2^{iii}	64.12(18)	N2^{ii}-Cu1-N2^{iv}	115.88(18)	N2^{ii}-Cu1-N2^{vii}	180.0(5)
N2^{ii}-Cu1-N2^{viii}	115.88(18)				

Symmetry transformations used to generate equivalent atoms:

(i) -x+1/4,y+1,-z+5/4; (ii) z,x+1/2,y-1/2; (iii) y-1/2,z+1/2,x; (iv) -y+1/2,-x+1/2,-z; (v) -x,-z+1/2,-y+1/2; (vi) -z,-y+1,-x; (vii) x-1/4,z+1/4,-y+1/2; (viii) z-1/4,-y+2,x-1/4; (ix) -x+5/4,-y+5/4,z+1; (x) z+1,-x+3/4,-y+3/4; (xi) -y+3/4,z+1/2,-x+5/4;

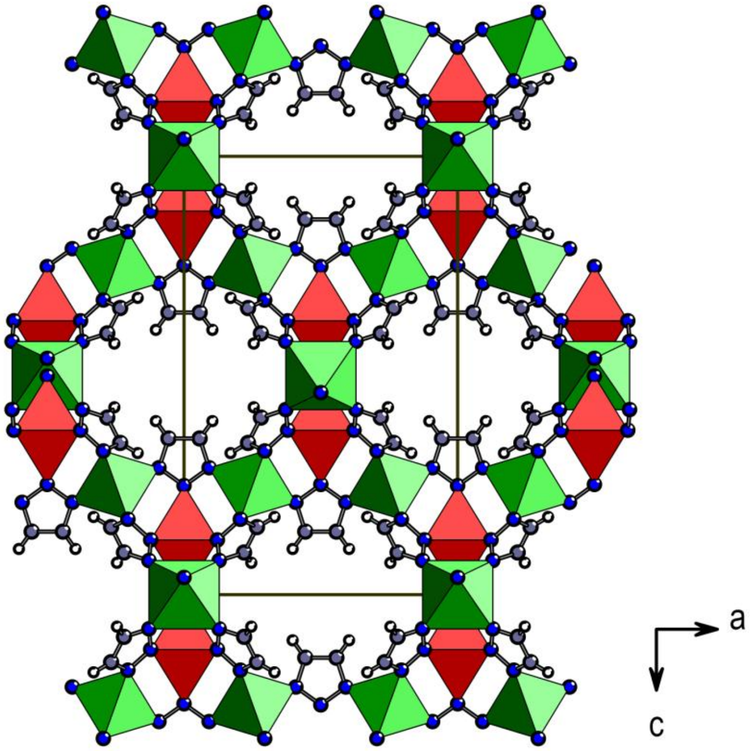

Fig. S1a. Packing diagram of **α**–[Cu(ta)$_2$], as viewed along *b*-direction.

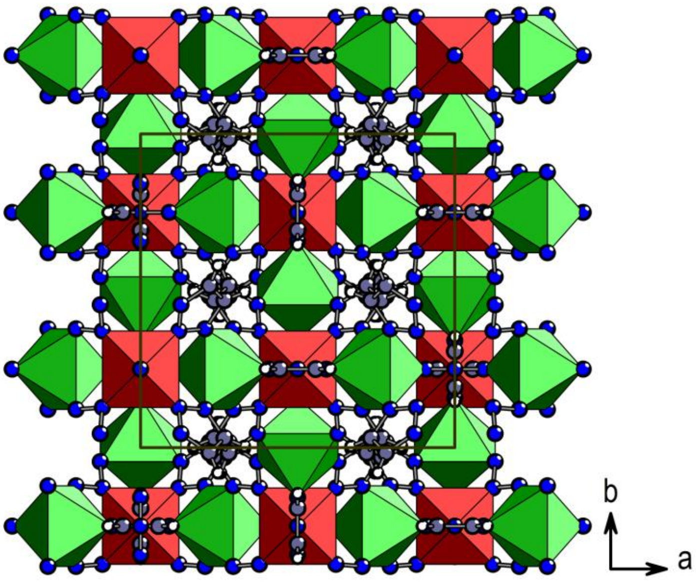

Fig. S1b. Packing diagram of **α**–[Cu(ta)$_2$], as viewed along *c*-direction.

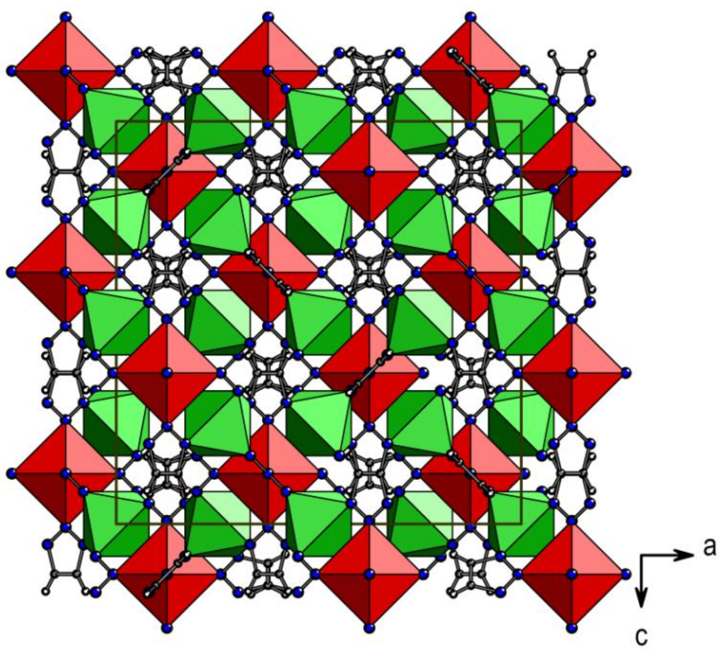

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Fig. S2a. Packing diagram of **β**–[Cu(ta)$_2$], as viewed along *b*-direction.

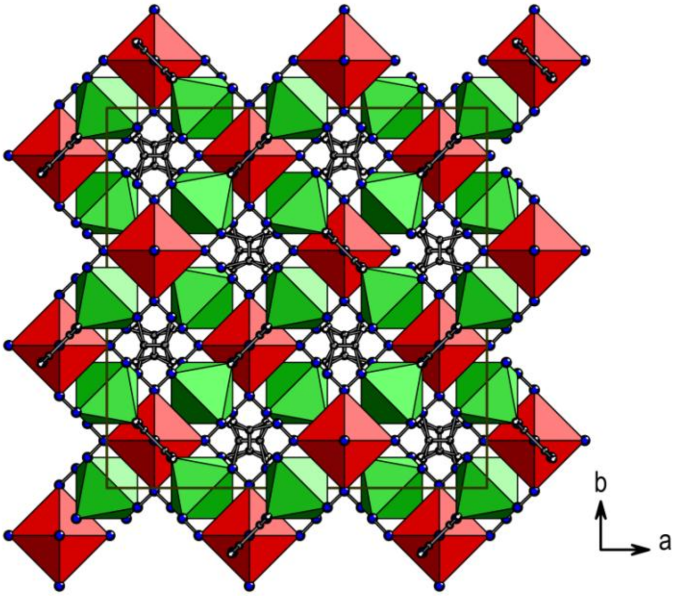

Fig. S2b. Packing diagram of **β**–[Cu(ta)$_2$], as viewed along *c*-direction.

Table S5. The intensity, area and peak positions of Bragg reflexes for **α**– and **β**–[Cu(ta)$_2$].

Temperature/°C	**Peak**	**Area**	**Position/°2θ**	**Width/°2θ**
160	(111)	3061.26	8.76	0.06
160 (after cooling)	(111)	3077.16	8.76	0.06
160	(311)	222.98	16.80	0.4
160 (after cooling)	(311)	225.38	16.80	0.4
160	(400)	247.59	20.30	0.17
160 (after cooling)	(400)	246.22	20.30	0.13

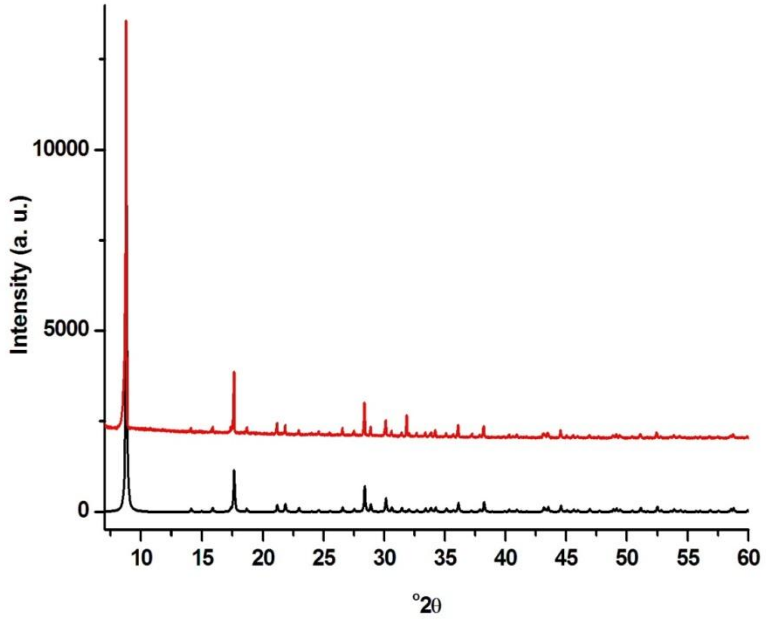

Fig. S3a. Calculated (black) and observed (red) powder patterns for **α**–[Cu(ta)$_2$].

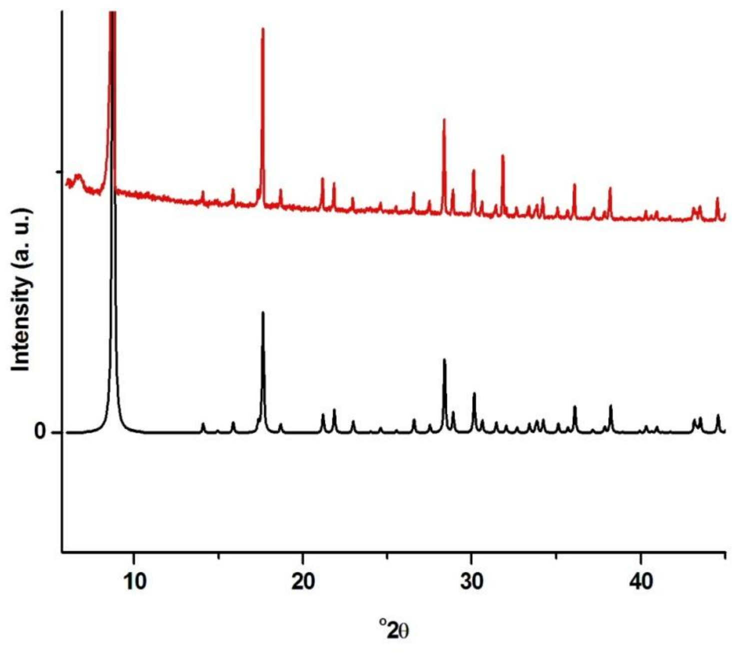

Fig. S3b. Calculated (black) and observed (red) powder patterns for **α**–[Cu(ta)$_2$] – expanded view in the range 6-45 °2θ.

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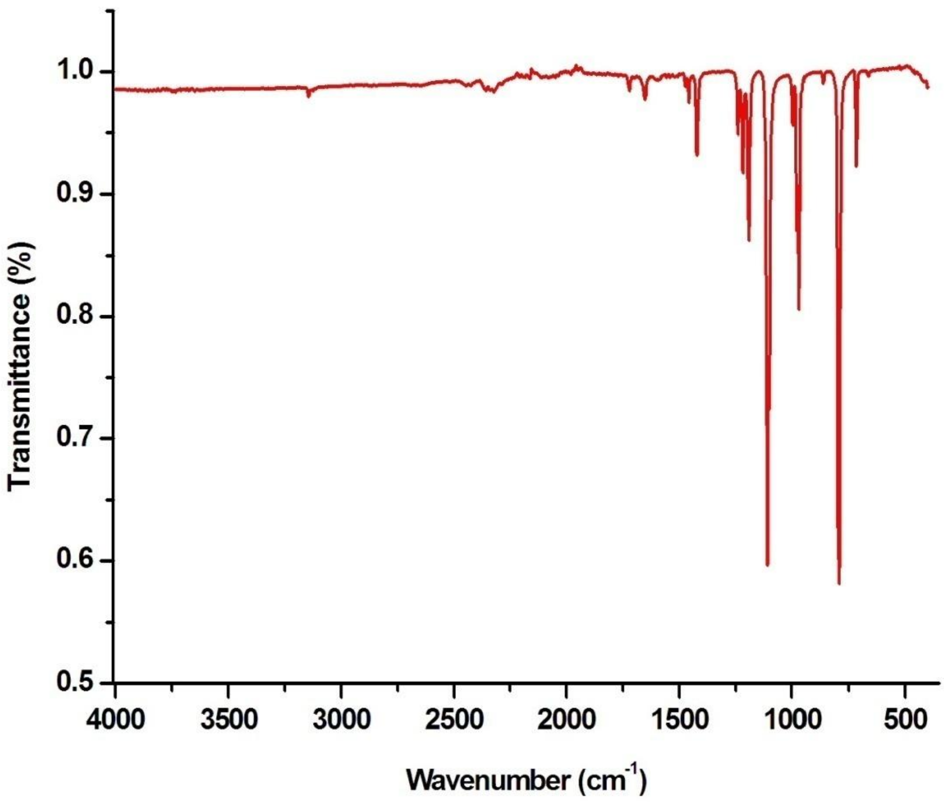

Fig. S4. IR spectrum of **α**–[Cu(ta)$_2$].

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